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TECHNICAL ASSISTANCE DOCUMENT FOR THE NATIONAL AMBIENT AIR TOXICS TRENDS AND ASSESSMENT PROGRAM

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TABLE OF CONTENTS

Page

Disclaimer ii
Acknowledgments iii
Acronyms and Abbreviations xvi

Section 1 Introduction 1

1.0 What is a Trends Monitoring Network and Why is it Important? 1
1.1 What is Data Consistency and Why is it Needed? 2
1.2 What is the CAA List and How Does it Relate to Trends Monitoring? 3
1.3 What are GPRA Goals and How Do They Relate to Trends Monitoring? 3
1.4 What is the Relationship between Health Risk Assessment and Air Toxics Compounds? 4
1.5 What are State and Regional Monitoring Goals and How Do They Relate to National Trends Monitoring Network? 4
1.6 EPA's Air Toxics Programs: Exposure/Risk Evaluation and Trends Analysis 5
1.7 Reasons for Conducting a Monitoring Program 5
1.8 NATA and the Role of Ambient Monitoring 6
1.9 Site Considerations 7
1.10 The NATTS Pilot Projects 7
1.11 Short Summary of Each Subsequent Chapter 11
Resources and References 12

Section 2 Issues Concerning Establishment of a Trends Network 1

2.0 Consistency of Data 1
2.1 Establishing Monitoring Objectives: The Role of Data Quality Objectives and the Quality Assurance Project Plan 2
2.2 Achieving Monitoring Objectives 3

Section 3 Guidelines for Development of Monitoring and Quality Assurance Plans 1

3.0 Elements of Sound Planning 1
3.1 Data Quality Objectives 6
3.1.1 DQOs for the NATTS Program 7
3.1.2 Application of the General DQO Process 9
3.1.3 Explain the Use of Method Quality Objectives in the Absence of DQOs, and Provide a Clear Distinction between MQOs and

Method Capabilities 15
3.2 Monitoring and Quality Assurance Project Plan Elements 15
3.2.1 Why are a Monitoring Plan and a QAPP Important? 16
3.2.2 How Specific Project Quality Objectives Would Complement DQOs for the NATTS Program 16
3.2.3 NATTS Quality System Description 18
3.2.4 How Specific Site Quality Objectives Would Complement Consistency between Sites in the NATTS Program 21
3.3 Hierarchy of QA Plan Levels 21
3.3.1 QA Project Plan Identification and Approval 22
3.3.2 Table of Contents 22
3.3.3 Distribution 22
3.3.4 Project/Task Organization/Roles and Responsibilities 22
3.3.5 Problem Definition/Background 23
3.3.6 Project/Task Description 23
3.3.7 Quality Objectives and Criteria for Measurement Data 23
3.3.8 Special Training Requirements/Certification 24
3.3.9 Documentation and Records 24
3.3.10 Project Description 24
3.3.11 Sampling Method Requirements 26
3.3.12 Sample Handling and Custody 27
3.3.13 Analytical Method Requirements 28
3.3.14 Quality Control Requirements 30
3.3.15 Instrument/Equipment Testing, Inspection, and Maintenance Requirements 31
3.3.16 Instrument/Equipment Calibration and Frequency 32
3.3.17 Inspection/Acceptance for Supplies and Consumables 32
3.3.18 Data Acquistion Requirements 33
3.3.19 Data Management 34
3.3.20 Assessments and Response Actions 36
3.3.21 Reports to Management 39
3.3.22 Data Review 40
3.3.23 Data Review, Verification and Validation Methods 40
3.3.24 Reconciliation with Data Quality Objectives 41
Resources and References 42

Section 4 Measurement Methods for the NATTS Program 1

4.0 Introduction 1
4.1 Overview of EPA Compendium Method TO-15 1
4.1.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities 2
4.1.2 Contamination 3

TABLE OF CONTENTS (Continued)

Page

4.1.3 Precision 4
4.1.4 Sampling Procedure and Issues Associated with EPA Compendium Method TO-15 5
4.1.4.1 Sample Inlet and Manifold 5
4.1.4.2 Sampling Equipment 10
4.1.4.3 Components of the Specified Sampling System 11
4.1.5 Canister Sampling System Certification 13
4.1.5.1 Certification Equipment 15
4.1.5.2 Certification Procedure 17
4.1.6 Canister Cleaning 19
4.1.6.1 Canister Cleaning Equipment 19
4.1.6.2 Canister Cleaning Procedure 23
4.1.6.3 Determination of Canister Cleanliness 25
4.1.7 Sample Collection Procedure 26
4.1.7.1 Specifications for the Sampling System 28
4.1.8 Analysis Procedures and Issues 29
4.1.8.1 Interferences 29
4.1.8.2 Chromatography Issues 30
4.1.8.3 Humidity 30
4.1.8.4 Equipment and Materials for VOC Analysis 33
4.1.8.5 Analytical Procedure 35
4.1.8.6 Preparation of the GC/MS Analytical System 38
4.1.8.7 Initial Calibration 39
4.1.8.8 Analytical Sequence 41
4.1.8.9 Sample Tracking 42
4.1.8.10 Sample Analysis 42
4.1.8.11 Sample Dilution 44
4.1.9 Requirements for Demonstrating Method Acceptability for VOC Analysis 44
4.1.9.1 Determination of Method Detection Limits 45
4.1.9.2 Replicate Precision 47
4.1.9.3 PE Accuracy 47
4.1.10 Quality Control Specifications 48
4.2 Overview of Compendium Method TO-11A 50
4.2.1 Sampling Procedure and Issues Associated with EPA Compendium Method TO-11A 53
4.2.1.1 O_3 Scrubbers 53
4.2.1.2 Denuder O_3 Scrubber 54
4.2.1.3 Cartridge O_3 Scrubber 57

TABLE OF CONTENTS (Continued)

Page

4.2.2 Sample Collection Systems 57
4.2.2.1 Sample Collection System Equipment 58
4.2.2.2 Carbonyl Sampling System Certification 59
4.2.2.3 Sample Collection Procedures 59
4.2.2.4 Collection System Specifications 61
4.2.3 Analysis Procedures and Issues 62
4.2.3.1 Analytical Interferences and Contamination 62
4.2.3.2 Extraction and Chromatography Issues 64
4.2.3.3 Sample Preparation 64
4.2.3.4 Preparation of the Analytical System 65
4.2.3.5 Process Blanks 67
4.2.3.6 Precision and Accuracy 69
4.2.3.7 Method Detection Limits 70
4.2.3.8 Sample Analysis 72
4.2.3.9 Method Spikes 72
4.2.3.10 Data Reduction, Validation and Reporting 75
4.3 Overview of EPA Compendium Method IO-3.5 76
4.3.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities (ICP/MS) 76
4.3.2 Sampling Procedures and Issues Associated with Method IO-3.5 76
4.3.2.1 Sample Collection Procedure 77
4.3.3 Analysis Procedures and Issues 79
4.3.3.1 Interferences and Contamination 80
4.3.3.2 Sample Preparation 81
4.3.3.3 Standard and QC Sample Preparation 83
4.3.3.4 Calibration 85
4.3.3.5 Internal Standards 86
4.3.3.6 Instrument Procedure 86
4.3.4 Quality Control 87
4.3.4.1 Precision 87
4.3.4.2 MDLs 88
4.3.4.3 QC Specifications 89
4.3.5 Instrument Operating Conditions 90
4.3.6 Analysis Procedure 91
4.3.7 Hexavalent Chromium Sampling and Analysis 93
4.3.7.1 Hexavalent Chromium Sample Collection 93
4.3.7.2 Hexavalent Chromium Analytical Method 94
4.3.7.3 Method Detection Limits 95

TABLE OF CONTENTS (Continued)

Page

4.3.7.4 QC Considerations 96
4.4 Overview of Semivolatile Organic Compounds Measurement 97
4.4.1 Sampling Procedures and Issues Associated with EPA Compendium Method TO-13A 97
4.4.1.1 Sampling Equipment and Materials 97
4.4.1.2 Sample Collection Procedures 98
4.4.2 Analysis Procedures and Issues 99
4.4.2.1 Interferences 101
4.4.2.2 Preparation of Reagents and Materials 102
4.4.2.3 Cleaning of XAD-2® 102
4.4.2.4 Preparation of a Sampling Cartridge 104
4.4.2.5 Reagents 105
4.4.2.6 Analytical Equipment 106
4.4.2.7 Sample Extraction, Concentration and Cleanup 107
4.4.2.8 Initial Calibration 108
4.4.2.9 Analysis of Samples 114
4.4.3 Determination of MDLs 116
4.4.4 Quality Control 119
4.4.5 Resolving Polycyclic Aromatic Hydrocarbons (PAHs) Only–An Alternative Approach 120
4.4.5.1 Sampling Apparatus and Procedures 123
4.4.5.2 Sample Collection Procedures 124
4.4.6 Analysis Procedures and Issues 125
4.4.6.1 Sample Extraction, Concentration and Cleanup 125
4.4.6.2 GC/MS Analysis 126
4.4.6.3 Determination of MDLs 128
4.4.6.4 QA/QC 130
4.5 Overview of EPA Compendium Method TO-9A 132
4.5.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities 135
4.5.2 Sampling Procedure and Issues Associated with EPA Compendium Method TO-9A 135
4.5.2.1 Sampling Procedure 136
4.5.3 Analytical Procedures and Issues 138
4.5.3.1 Equipment, Materials, Reagents and Standards 138
4.5.3.2 Sample Preparation 139
4.5.3.3 Interferences and Contamination 142
4.5.3.4 Preparation of the Analytical System 142
4.5.3.5 Determination of MDLs 144

TABLE OF CONTENTS (Continued)

Page

4.5.3.6 IC for Analysis of Field Samples 145
4.5.3.7 Analytical Procedure 149
4.5.3.8 Calculations 150
4.5.4 Quality Assurance/Quality Control 151
4.6 Aerosol Black Carbon Measurement Procedure 153
4.6.1 Overview of BC Measurement 154
4.6.2 General Description of Measurement Method 155
4.6.3 Interferences 156
4.6.4 Operational Procedure 157
4.6.4.1 Filtration Medium 157
4.6.4.2 Operating Protocol for BC with Magee Scientific Model AE-21 Aethalometer 161
4.6.5 Validation 165
4.6.6 Accuracy/Sensitivity 165
4.6.7 Data Processing 165
4.7 Overview of Meteorological Monitoring 167
4.7.1 System Specifications for Meteorological Measurements 168
4.7.1.1 Siting Considerations 169
4.7.1.2 Wind Speed and Wind Direction 172
4.7.1.3 Temperature 173
4.7.1.4 Atmospheric Humidity 175
4.7.1.5 Precipitation 176
4.7.1.6 Solar Radiation 177
4.7.1.7 Barometric Pressure 179
4.7.1.8 System Performance 179
4.7.2 Upper-Air Meteorological Monitoring 181
4.7.2.1 Siting and Exposure for Upper-Air Measurements 183
4.7.2.2 Tall Towers 183
4.7.2.3 Balloon Systems 184
4.7.2.4 Ground-Based Remote Sensors 185
4.7.2.5 System Performance 189
4.7.3 Estimation of Mixing Height 190
4.8 Innovative Methods for Ambient Air Monitoring with Potential for Future Application 192
4.8.1 Aldehydes and Ketones 192
4.8.1.1 Application of Modified EPA Compendium TO-11A Methodology to the Analysis of Acrolein and Crotonaldehyde 195

TABLE OF CONTENTS (Continued)

Page

4.8.1.2 Formaldehyde Continuous Monitors 196
4.8.2 Remote Sensing Applications 198
4.8.2.1 Optical Measurements of Trace Gases for NATTS 198
4.8.3 Particle Characterization: Photoacoustic Analyzer 201
Resources and References 202

Section 5 Data Management 1

5.0 Introduction 1
5.1 Data Consistency 1
5.2 Data Validation 2
5.3 Data Archiving 8
5.4 Data Entry into AQS 9
5.4.1 VOCDat 11
Resources and References 14

Appendix A DQOs for the Six Study Compounds 1

LIST OF TABLES

Page

1.1-1 NATTS Monitoring Requirements 8

3.1-1 Internet Sources for Methods Used in the TAD 5

3.1-2 Summary of Quality Control Criteria for NATTS Laboratory Analysis 29

4.1-1 Characteristic Masses Used for Quantitation of VOCs 31

4.1-2 4-Bromofluorobenzene (BFB) Tuning Criteria 35

4.1-3 Internal Standards and BFB: Characteristic Masses 36

4.1-4 Method Detection Limits for GC/MS Analysis of VOCs 45

4.1-5 Student's t Values at the 99% Confidence Level 47

4.1-6 Summary of Air Toxics TO-15 Quality Control Procedures 49

4.2-1 Carbonyl Compounds Measured Using EPA Compendium Method TO-11A 63

4.2-2 Student's t Values Used in Calculation of Method Detection Limits 71

4.2-3 MDLs for Carbonyl Data for the NATTS Program 71

4.2-4 Summary of Carbonyl Quality Control Procedures 73

4.3-1 Metals Measured Using EPA Compendium Method IO-3.5 80

4.3-2 MDLs for EPA Compendium Method IO-3.5 88

4.3-3 QCS for ICP/MS Analysis 89

4.4-1 SVOCs Measured for the NATTS Program Using the Procedures of EPA Compendium Method TO-13A 99

4.4-2 DFTPP: Key Ions and Ion Abundance Criteria 107

4.4-3 Quantitation Scheme for Semivolatile Organic Compounds According to Method 8270 109

LIST OF TABLES (Continued)

Page

4.4-4 Calibration Check Compounds for Analysis of SVOCs for the NATTS Program 112

4.4-5 MDLs for SVOCs Measured in the NATTS Program 117

4.4-6 Surrogate Compound Control Limits for SVOC Analysis Using EPA Compendium Method TO-13A/8270C 120

4.4-7 Student's t Values at the 99% Confidence Level 129

4.4-8 MDLs for EPA Compendium Method TO-13A Analytes: Extraction from Spiked PUF Using Hexane/Ether, Analysis Using SIM 130

4.5-1 Possible Number of Positional Isomers at Each Chlorine Level 132

4.5-2 Native and Isotopically Labeled Standards 137

4.5-3 Composition/Concentrations of the IC Solutions 146

4.5-4 QA/QC Requirements for EPA Compendium Method TO-9A Data 152

4.6-1 Aethalometer Specifications (Model AE-16-ER) for NATTS 158

4.7-1 Overview of Meteorological Monitoring Requirements 167

4.7-2 System Specifications for Surface Meteorological Measurements 168

4.7-3 Principles of Humidity Measurement 176

4.7-4 Classification of Pyranometers 178

4.7-5 Recommended System Accuracy and Resolution 180

4.7-6 Capabilities and Limitations of Meteorlogical Measurement Systems for Vertical Profiling of the Lower Atmosphere 182

4.7-7 Manufacturer's Specifications for Sensors Used in Rawinsondes 184

4.7-8 Functional Precision of Rawinsonde Measurements 185

LIST OF TABLES (Continued)

Page

4.7-9 Methods Used to Determine Mixing Heights 191

5.2-1 Manuals and Guides Available for EPA's AQS 10

LIST OF FIGURES

Page

3.1-1 General Quality System Components for NATTS Program 17

3.1-2 Operation of the NATTS Overall QA System 19

3.1-3 Example of Data Management and Sample Flow 35

4.1-1 Vertical Configuration 8

4.1-2 Horizontal Configuration 9

4.1-3 A Typical Multiple-Event Sample Collection System 12

4.1-4 Dedicated Manifold for Zero Gas Certification 15

4.1-5 Dedicated Manifold for Challenge Gas Certification 16

4.1-6 Schematic of a Canister Cleanup System 23

4.2-1 Cross-Sectional View of the Denuder O_3 Scrubber 56

4.6-1 Example of a Field Data Sheet for Aethalometer Measurements 164

5.2.1 A Time Series Plot Illustrating Acetylene, Ethylene, Ethane, and Propylene 6

5.2.2 A Scatter Plot Illustrating the Relationship between Benzene and Acetylene at a Site 6

5.2.3 A Fingerprint Plot Illustrating the Changing Concentration of Toluene Over Time at Hourly Intervals 8

Acronyms and Abbreviations

ACN	acetonitrile
ACS	American Chemical Society
AIRS	Aerometric Information and Retrieval System
amu	atomic mass unit
ANSI	American National Standards Institute
AQS	Air Quality Subsystem (of the Aerometric Information and Retrieval System)
ASE	accelerated solvent extraction
ASQ	American Society for Quality
ASQC	American Society for Quality Control
BC	black carbon
BFB	4-bromofluorobenzene
CAA	Clean Air Act
CARB	California Air Resources Board
CBL	convective boundary layer
cc, cm^3	cubic centimeter
CCB	continuing calibration blank
CCV	continuing calibration verification
CD	compact disk
CFR	Code of Federal Regulations
cm	centimeter
COC	chain of custody
Cr^{+6}, Cr^{VI}	hexavalent chromium
CV	coefficient of variation
dB	decibels
DDD	*p, p'*-dichlorodiphenyldichloroethane
DDE	*p, p'*-dichlorodiphenyldichloroethylene

DDT	*p*, *p'*-dichlorodiphenyltrichloroethane
DFTPP	decafluorotriphenylphosphine
DNPH	2,4-dinitrophenylhydrazine
DNSH	dansylhydrazine
DQA	data quality assessment
DQI	data quality indicator
DQO	data quality objective
EC	elemental carbon
ECD	electron capture detector
EI	electron ionization
EPA	U.S. Environmental Protection Agency
EPC	electronic pressure control
ER	extended range
ERG	Eastern Research Group, Inc.
eV	electron volts
FAA	Federal Aviation Administration
FID	flame ionization detector
FRM	Federal Reference Method
FTIR	Fourier transform IR
g	gram(s)
GACT	Generally Achievable Control Technology
GC	gas chromatograph/gas chromatography
GC/MS	gas chromatograph/mass spectrometer, gas chromatography/mass spectrometry
GPRA	Government Performance Results Act
HAP	hazardous air pollutant
Hg	mercury
HPLC	high performance liquid chromatography

HRGC	high resolution gas chromatography
HRMS	high resolution mass spectrometry
HS	high sensitivity
HSV	high standard verification
IC	initial calibration
IC	ion chromatography
ICB	initial calibration blank
ICP/MS	inductively coupled plasma/mass spectrometry
ICS	interference check standard
ICV	initial calibration verification
ID	identification
in.	inch(es)
IO	Inorganic (*EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*. EPA/625/R-96/01a)
IPA	instrument performance audit
IS	internal standard
KI	potassium iodide
kW	kilowatt
L	liter(s)
LCS	laboratory control standard; laboratory control spike
LIDAR	light detection and ranging
LFB	laboratory fortified blank
LIMS	Laboratory Information Management System
Lpm	liters per minute
LRB	laboratory reagent blank
MACT	Maximum Achievable Control Technology
m	meter(s)

mB	megabyte(s)
MB	method blank
MDL	method detection limit
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
MQO	method quality objective
MRRT	mean relative retention time
MS	mass spectrometer/mass spectrometry; matrix spike
MS/MSD	matrix spike/matrix spike duplicate
:g	microgram(s)
:L	microliter(s)
:m	micrometer(s)
:s	microsecond(s)
n	number
NAAQS	National Ambient Air Quality Standard
NAMS	National Air Monitoring Station
NATA	National Air Toxics Assessment
NATTS	National Air Toxics Trends Stations
ND	not detected
NERL	National Exposure Research Laboratory (EPA)
NESCAUM	Northeast States for Coordinated Air Use Management
ng	nanogram(s)
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
nm	nanometer

NMOC	nonmethane organic compounds
NO_x	oxides of nitrogen
NWS	National Weather Service
O_3	ozone
OAQPS	Office of Air Quality Planning and Standards (EPA)
OC	organic carbon
ORD	Office of Research and Development (EPA)
ORIA	Office of Radiation and Indoor Air (EPA)
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon, polynuclear aromatic hydrocarbon
PAMS	Photochemical Assessment Monitoring Stations
PBT	Persistent Bioaccumulative Toxics Initiative
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PDFID	preconcentration direct flame ionization detection
PE	performance evaluation
PFK	perfluorokerosene
pg	picogram(s)
PM	particulate matter
$PM_{2.5}$	particulate matter with an aerodynamic diameter # 2.5 :m
PM_{10}	particulate matter with an aerodynamic diameter # 10 :m
POC	parameter occurrence code
ppb	parts per billion
ppbC	parts per billion as carbon
ppbv	parts per billion (by volume)
ppmC	parts per million as carbon

ppmv	parts per million (by volume)
PSP	precision spectral pyranometer
psig	pounds per square inch gauge
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
QA	quality assurance
QAD	Quality Assurance Division (EPA)
QAPP	Quality Assurance Project Plan
QC	quality control
QCS	quality control specifications
radar	radio detection and ranging
RASS	radio acoustic sounding system
RB	reagent blank
RCA	recommendation for corrective action
RF	response factor
rms	root mean square
RPD	relative percent difference
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
RTD	resistance temperature detector
RTP	Research Triangle Park
scfm	standard cubic feet per minute
scm	standard cubic meters
scmm	standard cubic meters per minute
SD	standard deviation

SIM	selected ion monitoring
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
sodar	sound detection and ranging
SOP	standard operating procedure
SRM	standard reference material
SSQC	second source quality control
STI	Sonoma Technology, Inc.
STP	standard temperature and pressure
SVOC	semivolatile organic compound
TAD	technical assistance document
TCDD	tetrachlorodibenzo-*p*-dioxin
TCEQ	Texas Commission on Environmental Quality
TM	toxics monitoring
TMDL	Total Maximum Daily Load Initiative
TO	toxic organic (*EPA Compendium for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition. EPA/625/R-96/01b)
TSA	technical systems audit
TSP	total suspended particulate
TTU	Texas Tech University
UAM	urban airshed model
UATMP	Urban Air Toxics Monitoring Program
UATS	Urban Air Toxics Strategy
UV-DOAS	UV-differential optical absorption spectroscopy
VOC	volatile organic compound

Section 1
Introduction

In 2001 the United States Environmental Protection Agency (EPA) designed a national network for monitoring air toxics compounds present in ambient air. The objective of this monitoring is to generate ambient air data and to compile these data in an extensive air toxics database. The use of actual field measurements to compare and reconcile with estimates from source dispersion models will refine the model and ultimately allow a better overall estimate of population exposure. The ultimate goal of this and other parts of EPA's Air Toxics Monitoring Strategy is to assess health risks.

The purpose of this technical assistance document (TAD) is to provide guidance to support EPA regional, state, and local agencies responsible for the implementation of this national network, so that consistent high quality data are obtained for entry into the air toxics database.

1.0 What is a Trends Monitoring Network and Why is it Important?

A monitoring network to document the concentration of certain air toxics on a national scale is being developed to achieve EPA's trends assessment objectives. Data from EPA's national monitoring activities will establish an estimate of national average concentrations for these air toxics compounds, allow EPA to evaluate the need for new National Ambient Air Quality Standards (NAAQS), and establish associated limits.

Data from sites in this trends network will be used to identify the probability that long-term changes or trends in ambient air concentrations are occurring. Using this information, EPA, states, and local agencies can estimate changes in the risks of human exposure. These changes can then be used to anticipate changes in environmental policy and to establish a regulatory stance.

As part of the overall National Air Toxics Assessment (NATA) process, ambient air quality data are important to help assess the national toxics inventory and long-term hazardous air

pollutant (HAP) trends. Creation of satellite monitoring sites using identical monitoring approaches to the National Air Toxics Trends Monitoring Stations (NATTS) but at locations other than the NATTS monitoring sites is envisioned by establishing partnership with state and local agencies. For example, urban sites identified as high risk (such as schools located near HAP emission sources or urban sites located in the persistent downwind direction from high activity areas) might use NATTS monitoring approaches to quantify ambient conditions in the vicinity of these localized "hot spots."

1.1 What is Data Consistency and Why is it Needed?

The objective of the NATTS is to successfully detect trends in HAPs concentrations with uniform certainty across the national set of monitoring sites, at the targeted level (i.e., a coefficient of variation of 15% over a period of three years). Using a 1-in-6-day monitoring frequency, the monitoring approach must show a combination of precision, accuracy, and sensitivity appropriate for the concentration ranges at a set of fixed monitoring sites each selected with consistent siting criteria. With the exception of acrolein, this level of performance is currently substantiated for a limited number of HAPs that have been monitored successfully over several years. These HAPs have National Institute of Standards and Technology (NIST)-based calibration standards or equivalent and have standardized monitoring calibration procedures. Therefore, to ensure the success of the NATTS, the initial set of compounds to be monitored excludes some HAPs. This conservative approach essentially guarantees success in meeting the program objective for the selected HAPs but excludes some high risk HAPs. Review of the status of methods at intervals in the future will be used to determine the prospect of adding HAPs in subsequent stages of the NATTS.

1.2 What is the CAA List and How Does it Relate to Trends Monitoring?

Currently, 188 HAPs are regulated under the Clean Air Act (CAA). Air emissions of these HAPs may cause a wide variety of adverse ecosystem and health problems, including cancer, neurological effects, reproductive effects and developmental effects. Emissions from multiple sources, including major stationary, area, and mobile sources, result in population exposure to these air toxics compounds. In some cases the public may be exposed to an individual HAP. More typically, however, people experience exposures to multiple HAPs from many sources. Exposures result not only from the direct inhalation of HAPs, but also from multipathway exposures such as drinking water contaminated from airborne deposition of HAP-laden particles, deposition on skin, various routes to ingestion in contaminated food, etc. Since this document addresses an ambient air monitoring program, the focus is on airborne HAPs.

1.3 What are GPRA Goals and How do They Relate to Trends Monitoring?

EPA's current Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels in order to significantly reduce the risk of cancer and other serious adverse health effects caused by airborne toxics. That goal will be modified to focus on risk reductions associated with exposure to air toxics as new data and tools become available[1]. By the year 2020, EPA's goal is to eliminate unacceptable risks of cancer and other significant health problems from air toxic emissions for at least 95% of the population (relative to the population at the time of interest), with particular attention to children and other sensitive subpopulations, and substantially reduce or eliminate adverse effects on our natural environment.[2] No one specific level of risk is "unacceptable." Acceptability of risk is influenced by many factors. EPA identified lifetime excess risks of cancer of 100 in a million as being the upper end of the range of acceptable risk. Typically, the EPA treats environmental risks (either from a single source type or from a pollutant in an environmental medium) of 1 in a million or less as not being of regulatory concern. To evaluate progress toward EPA's goals, the first priority is to establish a baseline—what are air toxics levels *now*?—against which progress can be measured as successive years of monitoring data become available.

1.4 What Is the Relationship between Health Risk Assessment and Air Toxics Compounds?

EPA's ultimate goal is to eliminate unacceptable risks of cancer and other significant health problems from exposures to air toxics emissions and to substantially reduce or eliminate adverse effects on our natural environment. To provide a basis for decision making with respect to these matters, a NATTS network is being developed.

To make progress toward this risk-based goal, EPA will focus on:

- The cumulative health and ecosystem risks inherent in modern urban and rural living;
- The multimedia effects of air toxics on water bodies in which water quality and aquatic life are affected by the deposition of persistent and bioaccumulating air toxics;
- The multimedia effects of persistent air toxics deposition to soil (e.g., lead, dioxins); and
- The effects on sensitive populations and on economically disadvantaged communities. Are economically disadvantaged communities at a higher level of risk (i.e., more exposure, higher levels of exposure) than other types of communities?

1.5 What are State and Regional Monitoring Goals and How Do They Relate to National Trends Monitoring Network?

Ongoing and past regional, state, and local monitoring efforts have performed a twofold mission in ambient air toxics programs. First, existing monitoring sites have been selected to assess exposure and ambient air quality issues important to local communities. Local and regional goals have often focused on evaluation of exposure of particular groups of people to localized sources of HAPs. Second, the monitoring techniques used by these sites and the data generated through these monitoring programs also provide the basis for selection of a permanent, long-term national ambient air quality monitoring network.

1.6 EPA's Air Toxics Programs: Exposure/Risk Evaluation and Trends Analysis

In 1987, EPA developed the Urban Air Toxics Monitoring Program (UATMP) to help state and local agencies characterize the nature and distribution of potentially toxic air pollution in urban areas. The original intent of the UATMP was to screen ambient air samples for concentrations of toxic volatile organic compounds that could cause adverse human health effects. Since 1987, several state and local agencies have participated in the UATMP by implementing ambient air monitoring programs. These efforts have helped to identify the toxic compounds most prevalent in the ambient air and emissions sources likely to contribute to elevated concentrations. As a screening program, the UATMP also provides data input for models used by EPA, state, and local personnel to assess risks posed by the presence of toxic compounds in urban areas. The UATMP is a year-round sampling program, collecting 24-hour integrated ambient air samples every 12 days at urban sites in the contiguous United States.

In 1999, the EPA expanded the UATMP to provide for the measurement of additional HAPs to support GPRA. EPA and the states initiated pilot studies to determine the best candidate sites for a long-term air toxics monitoring network. The data obtained using a single, consistent approach for toxic monitoring and a comprehensive, program-specific Quality Assurance Project Plan (QAPP) allow EPA, state, and local risk assessors to evaluate the prevalence, concentration and trends for air toxics compounds in the urban air. The data collected continuously over a period of years produce consistent results for use by data analysts. Meeting method specifications with consistent approaches to sampling and analysis yields consistent and defensible data.

1.7 Reasons for Conducting a Monitoring Program

To address the concerns posed by air toxics emissions and to meet strategic goals, EPA has developed a National Air Toxics Program designed to characterize, prioritize, and address the impacts of HAPs on the public health and the environment. The National Air Toxics Program seeks to address air toxics problems through a strategic combination of several agencies' activities

and authorities, including regulatory approaches and voluntary partnerships. EPA envisions four key areas of activities:

- Source-specific standards and sector-based standards, including Section 112 standards, i.e., Maximum Achievable Control Technology (MACT), Generally Achievable Control Technology (GACT), residual risk standards, and Section 129 standards.

- National, regional, and community-based initiatives to focus on multimedia and cumulative risks, such as the Integrated Urban Air Toxics Strategy, Great Waters and National Estuary Program, Mercury Initiatives, Persistent Bioaccumulative Toxics (PBT) and Total Maximum Daily Load (TMDL) Initiatives, and Clean Air Partnerships.

- NATA activities to help EPA identify areas of concern, characterize human health and ecosystem risks and track progress. These activities include expanded air toxics monitoring, improving and periodically updating emissions inventories, national- and local-scale air quality and exposure modeling, and continued research on effects and assessment tools. These efforts will lead to improved characterizations of air toxics risk and reductions in risk resulting from ongoing and future implementation of air toxics emissions control standards and initiatives.

- Public education and outreach to focus public attention on the NATA activities. Application of a consistent program that maintains established standards for monitoring quality and performance will be critical to the success of all the other major areas of activities within the National Air Toxics Program.

1.8 NATA and the Role of Ambient Monitoring

A key component for the air toxics monitoring network is the designation of HAPs that will be measured. It is not practical to measure all HAPs at all locations. Recognizing the practical limitations on air toxics regulatory programs, the CAA amendments required EPA to develop a subset of the 188 toxics identified in Section 112 with the greatest impact on the public and the environment in urban areas. This subset of the 188 air toxics consists of the 33 HAPS identified in the Integrated Urban Air Toxics Strategy (UATS)[3] commonly referred to as the "Urban HAP List." Because this Urban HAP List was developed to reflect a variety of possible exposure periods (acute/chronic), pathways (inhalation, dermal, ingestion), and types of adverse health effects

(cancer/noncancer), the toxics monitoring network should attempt to address the full Urban HAP List. Considering the chemical properties of these HAPs, they can be grouped into several general categories, including volatile organic compounds (VOCs), metals, aldehydes, and semivolatile organic compounds (SVOCs).

From the Urban HAP List of 33 HAPs, candidates for the NATTS Program were selected and are presented in Table 1.1-1. Six of the 20 entries in Table 1.1-1 must be monitored from the initiation of NATTS because these entries are the major risk drivers based on a relative ranking performed by EPA. The remaining 14 entries must be reported to NATTS if the corresponding methods are being conducted at the site.

1.9 Site Considerations

Information on air toxics compounds is needed for both urban and rural areas. Urban-oriented information is needed to address the range of population exposures across and within urban areas, whereas rural data are needed for characterization of exposures of nonurban populations, to establish background concentrations and to better assess environmental impacts. The monitoring sites needed to accomplish NATTS Program goals must emphasize long-term measures of air quality. NATTS Program monitoring data must focus on long-term, year-round information. Therefore, NATTS Program participants must use monitoring sites established and maintained in the same location and collect data year-round for many years using the methods and frequency guidelines specified in this TAD. For manual sampling, the default frequency for sample collection at NATTS Program collection locations is one sample every six days, as determined by the requirements of the NATTS data quality objectives (DQOs).

1.10 The NATTS Pilot Projects

The success of the NATTS Program depends critically on EPA's ability to understand and quantify the impacts of air toxics emissions on public health and the environment. To that

Table 1.1-1. NATTS Monitoring Requirements

NATTS Year 1 **These monitoring requirements must be implemented from the initiation of NATTS monitoring because these compounds are the major risk drivers.**		
Monitored	**Method**	**UATMP Element[3]**
benzene	TO-15	yes
1,3-butadiene	TO-15	yes
arsenic (As) compounds	IO-3.5	yes
hexavalent chromium (Cr^{+6})	Research Method	yes
formaldehyde	TO-11A	yes
acrolein[1]	Research Method	no
NATTS **VOCs listed below must be reported and considered as NATTS compounds if Method TO-15 is being applied. Metals must be reported and considered as NATTS elements if Method IO-3.5 is being applied. Carbonyl Compounds listed below must be reported and considered as NATTS compounds if Method TO-11A is being applied.**		
VOCs		
carbon tetrachloride	TO-15	yes
chloroform	TO-15	yes
1,2-dichloropropane (propylene dichloride)	TO-15	yes
methylene chloride (dichloromethane)	TO-15	yes
tetrachloroethylene (perchloroethylene, PCE)	TO-15	yes
trichloroethylene (TCE)	TO-15	yes
vinyl chloride	TO-15	yes
Metals		
beryllium (Be) and compounds	IO-3.5	yes
cadmium (Cd) and compounds	IO-3.5	yes
chromium (Cr) and compounds[2]	IO-3.5	yes
lead (Pb) and compounds	IO-3.5	yes
manganese (Mn) and compounds	IO-3.5	yes
nickel (Ni) and compounds	IO-3.5	yes
Carbonyl Compounds		
acetaldehyde	TO-11A	yes

[1] Modifications to the TO-11A methodology being evaluated. Sampling and analytical methodology using dansylhydrazine as a derivatizing reagent also being evaluated.

[2] Method IO-3.5 measures Total Chromium only; determination of hexavalent chromium requires a specialized sampling and analytical methodology.

[3]Accepted sampling and analytical methodology is presently available through EPA's UATMP.

end, EPA has already initiated numerous NATTS Program activities. All of these activities are aimed at providing the best current technical information regarding air toxics emissions, ambient concentrations, and health and environmental impacts to support the development of sound policies for a National Air Toxics Program. Specifically, ambient monitoring data are needed to characterize air toxics ambient concentrations and toxics deposition to better understand the fate and transport of air toxics in the atmosphere and to help evaluate atmospheric dispersion and deposition models. Because it is impractical to monitor everywhere, modeled estimates are needed to extrapolate knowledge of air toxics impacts into locations without monitoring. A combination of reliable modeling systems along with well-designed ambient networks is the best approach for estimating ambient concentrations and population/ecosystem exposure across the nation.

EPA and its state and local partners have developed and implemented pilot toxics monitoring (TM) projects as an element of the NATTS Program.[4] The pilot TM projects were designed:

- To refine monitoring approaches;
- To provide data to allow determination of DQOs for NATTS; and
- To characterize, prioritize, and address the impacts of HAPs on the public health and the environment.

The pilot TM projects typically include multiple sites in a localized network. EPA strives to establish the ability to better define residual risks and determine the additional controls that may be needed to address toxic pollutant emissions. This better definition is being addressed through the continuing development of the National Toxics Inventory and added emphasis on air toxics monitoring.

The pilot TM projects are comprised of four key elements:

- Source and sector based standards;
- National, regional, and community-based initiatives that focus on multimedia and cumulative risks;
- Ongoing education and outreach; and
- NATAs.

NATAs are intended to help identify key areas of concern and track performance. Assessment activities include:

- Expanded air toxics monitoring;
- Improving and periodically updating emissions inventories;
- Multilevel air quality and exposure modeling; and
- Continued research on effects and assessment tools.

The specific objectives of the pilot TM projects are as follows:

- To provide a database sufficient to optimize the implementation of the NATTS Program;
- To characterize pollution gradients reflecting diverse population areas and a variety of emission sources;
- To provide information on concentration levels and pollutant type variability to compare with model outputs;
- To obtain data to determine the number of sites and the collection frequency (see Section 3.1.1, DQOs for the NATTS Program, for a discussion of collection frequency) required to appropriately characterize the state of air toxics pollution in individual urban areas; and
- To determine the range of concentrations that may be expected in differing urban/rural environments and source influences (i.e., mobile sources, industrial activity, normal background, etc.).

In addition, initial new monitoring together with data analysis from existing measurements will be needed to provide a sufficient understanding of ambient air toxics concentrations throughout the country in order to decide on the appropriate quantity and quality of needed data.

1.11 Short Summary of Each Subsequent Chapter

The remainder of this technical assistance document incorporates the following sections:

- "Issues Concerning Establishment of a Trends Network" (Section 2) includes guidance and rationale for consistency in site selection, sample collection and analysis procedures to ensure that DQOs for exposure assessment and trends are met.

- "Guidelines for Development of Monitoring and Quality Assurance Plans" (Section 3) includes the general approach and specific requirements for consistency in the quality control and quality assurance recommended for the NATTS monitoring. This section provides a brief discussion of data quality objectives and the fundamental components of site-specific QAPPs. Specific method quality objectives are provided for sample analysis procedures.

- "Measurement Methods" (Section 4) describes the consistent application of existing methods for the collection and analysis of NATTS Program samples, with specifications to restrict flexibility and resolve ambiguities in the Compendium Methods used for NATTS Program monitoring.

- "Data Validation and Management" (Section 5) provides guidance for data review and consistency. This section provides information and guidance on procedures to ensure data are consistent, validated, reported, archived and entered into the Aerometric Information Retrieval System-Air Quality Subsystem (AIRS-AQS) database in a consistent and equivalent manner for each of the participating NATTS participants.

Section 1: References and Resources

1. Peer Review Draft for the Science Advisory Committee, Air Toxics Monitoring Strategy Subcommittee FY-00. Air Toxics Monitoring Concept Paper. February 29, 2000. Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/cncp-sab.pdf

2. Final FY 2003 Technical Program Guidance; U.S. Environmental Protection Agency, Office of Air and Radiation, May 6, 2002.

3. Smith, R.L.; French, C.L.; Murphy, D.L.; Thompson, R. *Selection of HAPs Under Section 112(k) of the Clean Air Act: Technical Support Document*; Integrated Urban Air Toxics Strategy (UATS), July 28, 1999.

4. *Pilot City Air Toxics Measurements Summary*; EPA454/R-01-003; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. Available at http://www.epa.gov/ttnamti1/files/ambient/airtox/toxics2a.pdf

Section 2
Issues Concerning Establishment of a Trends Network

Current EPA GPRA commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels in order to significantly reduce the risk to Americans of cancer and other serious adverse health effects caused by airborne air toxics. To assess progress toward that goal, EPA has initiated numerous activities aimed at providing the best technical information regarding air toxics emissions, ambient concentrations, and health impacts. One key element of the full air toxics assessment process is the long-term monitoring of ambient concentrations of air toxics compounds at sites throughout the nation using consistent techniques to allow analysis of patterns and trends in ambient air toxics measurements.

2.0 Consistency of Data

The ability to detect and assess trends on a nationwide basis relies upon standardized operation of the NATTS Program based upon two key components:

- Strict and specific DQOs for the program; and
- Stability of a monitoring site including its location, measurement techniques, and its operations over the specified period of time to allow evaluation of trends.

Standardization of operations will yield consistency of data among the sites included in a monitoring network to allow evaluation of trends nationwide. To provide data usable for establishing trends at a given area, a monitoring site must be operating in the same location for an extended period of time (i.e., years). To know within the specified limits of error whether the concentrations of air toxics compounds have decreased by 75% in a given urban area since 1993, the same site must be performing the same measurements at the same frequency from 1993 (the baseline year) until the present. To perform a nationwide evaluation of trends, consistency of data among all of the sites in the monitoring network is essential: monitoring sites must be performing the same measurements using identical sampling and analytical methods in the same way over the

specified long-term period, meeting the same quality specifications and reporting data in the same way. The only way to achieve this consistency is through standardization of the methodology. All of the monitoring agencies must be performing the same measurements in the same way and meeting the same quality specifications. Even if the same siting criteria, measurement procedures, and analytical procedures are used, variability will still be introduced into the data set because there are different laboratories analyzing the samples using the same methods. Preliminary pilot study data will assess the relative proportions of the variability introduced by different collection equipment and analysis at different laboratories. The impact on overall data consistency of different collection equipment, laboratories, and reporting practices must be established and this impact minimized. The function of this guidance document is to provide the guidelines for standardization of the sampling, analytical, quality assurance, and reporting methodology.

2.1 Establishing Monitoring Objectives: The Role of Data Quality Objectives and the Quality Assurance Project Plan

The components essential to the systematic planning process that will result in monitoring data of the quality and quantity required to achieve program goals are DQOs and a QAPP. The project DQOs provide the answer to the critical question of how good the data must be in order to achieve Program goals. DQOs are used to develop the criteria that a data collection design should satisfy, including when to collect samples, where to collect the samples, the tolerable level of decision errors for the study, and how many samples to collect. Using the DQO process assures that the type, quantity, and quality of environmental data used in decision making will be appropriate for the evaluation of national trends in ambient air toxics measurements. DQOs for the overall trends monitoring network are determined by EPA. Individual monitoring sites may have additional DQOs as dictated by local priorities, but local DQOs cannot be less stringent than the EPA DQOs.

EPA policy requires that all projects involving the generation, acquisition, and use of environmental data be planned and documented and have an Agency-approved QAPP prior to the start of data collection. The primary purpose of the QAPP is to provide an overview of the

project, describe the need for the measurements, and define quality assurance/quality control (QA/QC) activities to be applied to the project, all within a single document. The QAPP should be sufficiently detailed to provide a clear description of every aspect of the project and include information for every member of the project staff, including site operators, laboratory staff, and data reviewers. The QAPP facilitates communication among clients, data users, project staff, management, and external reviewers. Effective implementation of the QAPP assists project managers in keeping projects on schedule and within the resources budgeted. State and local organizations must develop their own QAPPs that meet their specific needs.

2.2 Achieving Monitoring Objectives

The monitoring network must be designed to address all the needs of the NATTS Program and to satisfy the following objectives:

- Measure the pollutants of concern to the NATTS Program. As shown in Table 1.1-1, monitoring approaches for the pollutants of concern to the NATTS Program exist and are regularly being applied through the UATMP, with the exception of acrolein.

- Ensure nationally consistent data of high quality. To ensure nationally consistent data of high quality, the correct execution of specific sampling and analytical methodology is required. The methods selected must consider the threshold concentrations at which adverse health effects have been documented and provide sufficient sensitivity to provide an adequate limit of detection. The field and laboratory monitoring protocols must provide for adequate quality assurance and data management, including reporting practices.

- Collect a sufficient amount of data to estimate annual average concentrations at each monitoring site. A general guideline to estimate annual average concentrations at each monitoring site is to collect a minimum of one 24-hour sample every six days, a regime that will result in at least 61 samples per year, together with the requisite number of duplicates, replicates, etc. For a particular pollutant, however, the amount of data that is sufficient will depend on the estimated precision and accuracy of the monitoring method. Guidance on the method precision and accuracy that will be required will follow from the DQOs established by EPA.
- Complement existing programs. The NATTS Program network will be integrated with existing programs to achieve efficiencies of scale to the extent that

methodologies are compatible. The NATTS Program will maximize the use of existing platforms and take advantage of mobile monitoring and saturation monitoring resources, where appropriate.

- Reflect community-oriented population exposure. Stationary monitors should be sited to be representative of average concentrations within a 0.5- to 4-kilometer (km) area (i.e., neighborhood scale). These neighborhood-scale measurements are more reflective of typical population exposure, can be used to estimate long-term population risk, and should be the primary component of the NATTS Program. Whatever the scale of measurement, the monitors should represent typical population exposure as well as exposure in communities near air toxics emission sources that may be impacted disproportionately.

- Represent geographic variability. A truly national network must represent a variety of conditions and environments that will allow characterization of different emissions sources and meteorological conditions. This NATTS Program would support population risk characterization, understanding of the relationships between emissions and air quality under different circumstances, and allow for tracking of changes in emissions. National assessments should reflect the differences among cities and between urban and rural areas for selected HAPs, so the network should:

    — Include cities with high population risk (both major metropolitan areas and other cities with potentially high anticipated air toxics concentrations);

    — Distinguish differences within and between geographic regions (to describe characteristics of areas affected by high concentrations vs. low concentrations);

    — Reflect the variability among pollutant patterns across communities; and

    — Include background monitoring.

The initial focus of the NATTS Program on community-oriented locations will provide a population-oriented approach analogous to the core network for particulate matter with an aerodynamic diameter of # 2.5 :m ($PM_{2.5}$) and the basis for the National Air Monitoring Station (NAMS) trend network for the criteria pollutants. The NATTS Program will emphasize fixed station, long-term monitoring to allow the assessment of trends.

Section 3
Guidelines for Development of Monitoring and Quality Assurance Plans

Site-specific NATTS monitoring plans and associated QA program elements for field and laboratory efforts, as approved by EPA, are designed to ensure data consistency across the entire NATTS Program network. The guidance in this section is a resource for EPA Regional, state and local field and laboratory staff to use in developing specific plans for monitoring and QA that meet NATTS Program requirements, with references to complete documents.

EPA's requirement for a quality program for NATTS Program participants originates with EPA Order 5360.1 A2 (EPA 2000a) and the applicable Federal regulations that require a quality system for all EPA organizations and organizations funded by EPA that acquire environmental data through sampling and analysis. EPA policy is based on the national consensus standard, American National Standards Institute/American Society for Quality Control (ANSI/ASQC) E4-1994, *Specifications and Guidelines for Environmental Data Collection and Environmental Technology Programs,* developed by the ANSI and the American Society for Quality (ASQ).

3.0 Elements of Sound Planning

Systematic planning is a key project-level component of the NATTS Program Quality System. Quality planning starts with development of DQOs and continues with the items listed below:

- Community-oriented (i.e., neighborhood-scale) population exposure

  The initial focus of local NATTS Program sites should be on community-oriented locations, a population-oriented approach analogous to the core network for $PM_{2.5}$ and the basis for the NAMS trend network for the criteria pollutants.

To evaluate neighborhood-scale population exposure, fixed site (stationary) sampling equipment should be sited to be representative of average concentrations within a 0.5- to 4-km area (i.e., "neighborhood-scale"). Such measurements are more reflective of typical population exposure, can be used to estimate long-term population risk and should be the primary component of the NATTS Program. Separate sampling efforts may focus on smaller scale (i.e., middle or microscale) monitoring sites. For all scales of measurement, the samples collected should represent typical population exposure as well as exposure in communities near air toxics emission sources that may be disproportionately impacted.

Initially, the network should place a minimum of two sites in a variety of metropolitan areas unless appropriate historical data exist to allow identification of an appropriate monitoring site. With two sites, one site should reflect maximum population-oriented concentration for at least a subset of the target HAPs, perhaps in urban/industrial areas in which populations live near major sources. The second site should be reflective of "typical" high concentrations in areas with high population density to reflect relatively high exposure and population risk. These "typical" sites should be several miles away from major point sources and may represent the average-case scenario. Both types of sites can be used for emission tracking, emission inventory corroboration and model validation. When an area has only one site, that site should be more representative of average exposure.

- Long-/short-term monitoring elements

The NATTS Program will focus on long-term monitoring sites. The mature network could have approximately 100 trend sites among a total of 200 to 300 air toxics monitoring sites. The NATTS Program must emphasize fixed station, long-term monitoring but also contain short-term monitoring elements to enable the network to assess the multiple objectives of the toxics program. The network can be modeled after the existing State and Local Air Monitoring Stations (SLAMS). A SLAMS network includes long-term NAMS to study trends and pollutant impacts in major metropolitan areas, as well as other SLAMS monitoring stations to address state-level characterizations and assessments on a 3- to 5-year time frame.

The NATTS program should include monitoring to support short-term, area-specific studies. An example of short-term monitoring is characterization of "hot spot" communities potentially impacted by specific sources or specialized long-term monitoring to meet state needs. Such monitoring may utilize temporary or mobile monitoring stations and be an adjunct to the network of fixed site monitoring locations. These activities can be useful to facilitate proper assessments of geographic variability, both between and within metropolitan areas and permit development of hourly ambient concentrations for certain HAPs that may present acute threats at specific locations and times. The collection of on-site meteorological data would be useful to assist with these assessments.

- Make use of existing state and local platforms for the first two years of monitoring

  To initiate the NATTS Program, the new air toxics monitoring sites should build upon existing state and local air toxics monitoring sites, Photochemical Assessment Monitoring Stations (PAMS) sites or planned particulate matter (PM) chemical speciation sites to the extent that the existing sites incorporate methodologies that reflect the configurations and approaches presented in Section 4 of this document. Data consistency for NATTS is still a primary goal.

  PAMS sites are appropriate platforms for air toxics monitoring because they reside in the largest metropolitan areas and the "Site Type 2" is sited in the area of maximum ozone precursor concentrations. PAMS sites already include measurement of 8 HAP VOCs including benzene and usually two aldehydes. The Type 2 PAMS sites are on the downwind edge of an urban area, reflective of a neighborhood monitoring scale.

  $PM_{2.5}$ speciation trend sites also reflect community-oriented monitoring sites. These sites provide fine particle measurement of 10 of the 11 HAP metals (including the seven or eight metals in the UATS) and offer other air toxics pollutant-related sampling equipment such as particulate matter with an aerodynamic diameter of #10 :m (PM_{10}) and total suspended particulate (TSP) samplers. The latter provide opportunity for additional analysis for lead and other HAPs associated with larger particles. Other excellent choices for air toxics monitoring platforms are sites in the $PM_{2.5}$ supersite network. This network provides monitoring stations including a variety of routine and research grade gaseous and PM analyzers, many of which directly relate to the measurement of HAPs.

  The development of the NATTS Program should allow flexibility in the selection of monitoring locations and cities that satisfy the stated monitoring objectives. If existing platforms are not suitable for characterization of population exposure to air toxics, new community-oriented monitoring stations should be established. For example, some Type 2 PAMS sites may not be the best locations for measuring air toxics compounds because of the relative mix and spatial distribution of point and mobile emission sources in these areas. In addition, the Type 2 sites are located for summertime meteorological conditions and may not ideally represent maximum annual average concentrations or year-round exposure. Nevertheless, general siting criteria for PAMS Site Type 2 and $PM_{2.5}$ core monitoring stations can be followed when establishing the desired neighborhood-scale air toxics monitoring sites. These guidelines provide specifications on setback distances, inlet heights and other siting considerations.

- Utilize standard measurement approaches

Standardized measurement approaches must be used. Currently, there are recognized methods or approaches that cover 29 of the 33 UATS HAPs. The standard methods are listed below and described in Section 4. Network access for these methods is summarized in Table 3.1-1.

— EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry";

— EPA Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography";

— EPA Compendium Method TO-13A (for sample collection) / EPA SW-846 Method 8270 (for sample analysis), "Adapted Method for Determination of Semivolatile Organic Compounds in Ambient Air";

— EPA Compendium Method IO-3.5, "Determination of Metals of Ambient Particulate Matter Using Inductively Coupled Argon Plasma/Mass Spectrometry"; and

— EPA Compendium Method TO-9A, "Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans in Ambient Air."

HAPs that are not generally considered practical for monitoring studies include dioxins and furans (i.e., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, dioxin congeners and 2,3,7,8-tetrachlorodibenzofuran and dibenzofuran congeners). HAPs that lack a standard or demonstrated method include hydrazine, quinoline, acrolein and coke oven emissions as well as diesel emissions. Research is needed to develop new or more cost-effective monitoring methods to permit the measurement of more HAPs. Individual network sites should implement measurements of the additional five HAPs that are not generally considered practical as resources and methods become available. This monitoring becomes an important adjunct activity to the overall ambient air toxics monitoring strategy. More information on the developing methods is provided in Section 4. Existing methods should be used to the full range of their capabilities to optimize the coverage for HAPs.

Table 3.1-1. Internet Sources for Methods Used in the TAD

EPA Method	Reference	Title
EPA Compendium Method TO-9A	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-9arr.pdf	Determination of Polychlorinated, Polybrominated, And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air
EPA Compendium Method TO-11A	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf	Determination of Formaldehyde In Ambient Air Using Adsorbent Cartridges Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]
EPA Compendium Method TO-12	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-12.pdf	Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)
EPA Compendium Method TO-13A	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-13arr.pdf	Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)
EPA Compendium Method TO-15	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf	Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)
EPA Compendium Method TO-16	http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-16r.pdf	Long-Path Open-Path Fourier Transform Infrared Monitoring Of Atmospheric Gases
EPA Compendium Method IO-3.5	http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf	Determination of Metals In Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)
EPA Method 8270C	http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf	Method 8270C. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
EPA Method 3540C	http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3540c.pdf	Method 3540C. Soxhlet Extraction

- Provide resources for data analysis

  EPA will allocate resources for data analysis on an annual basis to ensure implementation of appropriate and consistent statistical quality assurance procedures, data management and data reporting to enhance data quality for an effective air toxics trends monitoring system. Data analysis protocols may include risk assessments, source attribution, trends analysis, etc. End user data analysis requirements have been used to develop the network DQOs and secondary uses of the data should be performed only after a review to determine whether the original data quality is sufficient for the secondary data use.

- Review the network periodically

  The national network will evolve and will be modified as needed. Annual technical systems audits of the network will be performed by each region on the NATTS sites under their purview. These audits will then be reviewed by EPA and adjustments will be made to eliminate redundancy of measurement within and across cities, to modify sampling frequency and to adjust implementation of measurement protocols to ensure that DQOs are achieved. The target list of pollutants should be modified to make cost-effective use of available resources while satisfying the goals of the air toxics program. In some cases, an analysis of subsets of the list of urban air toxics may be more appropriate. In particular, if a specific analyte requires its own discrete monitoring method and is not detectable at a site, that analyte can be eliminated from routine sampling and analysis. Eliminating individual analytes does not apply to compounds that are a part of a suite of compounds generated with a particular monitoring method (i.e., EPA Compendium Methods TO-15 or IO-3.5). However, the elimination of monitoring for compounds not detected should be periodically revisited to ensure that new emission sources (or better monitoring technologies) have not developed. Periodic checks for analytes eliminated from routine monitoring should be performed once every 3 - 5 years.

3.1 Data Quality Objectives

DQOs are qualitative and quantitative statements to clarify study objectives, define the appropriate types of data, and specify tolerable error of decisions that will be made from the data. Initial planning is required for ambient air monitoring programs to enhance consistency between sites, starting with common goals developed using the DQO Process[1].

3.1.1 DQOs for the NATTS Program

The Data Quality Objective (DQO) process provides a general framework for ensuring that the data collected by EPA meets the needs of decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet a program's goals The result of the DQO process is a series of requirements used as the basis for the detailed planning in a project-specific QAPP. The DQO process was applied to one of the primary goals of the National Air Toxics Monitoring Network, namely:

To be able to detect a 15% difference (trend) between two successive 3 -year annual mean concentrations within acceptable levels of decision error.

Being able to detect this trend would allow one to evaluate the effectiveness of HAP reduction strategies. This is not to say that the NATTS data can not be used for other purposes, just that the development of the quality system, data quality indicators and their resultant measurement quality objectives were based upon detecting the trend mentioned above. This section will provide a general description of the NATTS DQO process. Appendix A provides a more detailed explanation.

In order to develop the DQOs for the NATTS one needed to:

- Develop a data base and a model of the toxics compounds of interest.
- Identify the input parameters that are used to generate the model and effect the quality of the resultant concentration information
- Develop performance curves that marry the input parameters and a decision makers tolerance for decision errors.

Data Base and Model

Since it would not be feasible to develop DQOs for every toxic compound measured in the NATTS and it was a goal to establish as much simplicity and consistency in the measurement quality objectives as possible, six toxics compounds: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde were selected for the development of the DQOs.

Throughout this section, the term *decision maker* is used. This term represents individuals that are the ultimate users of ambient air data and therefore may be responsible for such activities like determining trends, HAP reductions or developing reduction strategies. The DQOs will be based on the data requirements of the decision maker(s). Decision makers need to be able to determine whether or not the data available for a decision are of adequate quality for their intended use and set limits on the probabilities of making incorrect decisions. These probability limits can be thought of as "comfort zones". Since all data have some level of uncertainty, the decision maker(s) needs to establish the zone that they feel comfortable with the potential uncertainties that may lead to an inappropriate decision.

Two types of uncertainties need to be recognized; population uncertainty and measurement uncertainty. Population uncertainty is defined as the natural spatial and temporal variability in the population of the data being evaluated. Measurement uncertainty is associated with the data collection process and is identified by the data quality indicators of precision, bias and completeness. In general, as one proceeds through the DQO process, the data quality indicators of precision, bias and completeness can be manipulated in order to achieve the required DQOs. Both population and measurement uncertainties are used in the DQO process as input parameters from which decision performance curves are generated. The performance curve graphically displays the quality of the decision process by showing the probability that environmental data will lead us to a given decision as a function of unknown truth. Using the performance curves allows one to input various values for the population and measurement uncertainties and helps to identify which of the uncertainties effect decision errors the most.

Figure 3.1 presents an example of the performance curve where an action limit of 15% difference is established. A number of items on this graph should be explained.

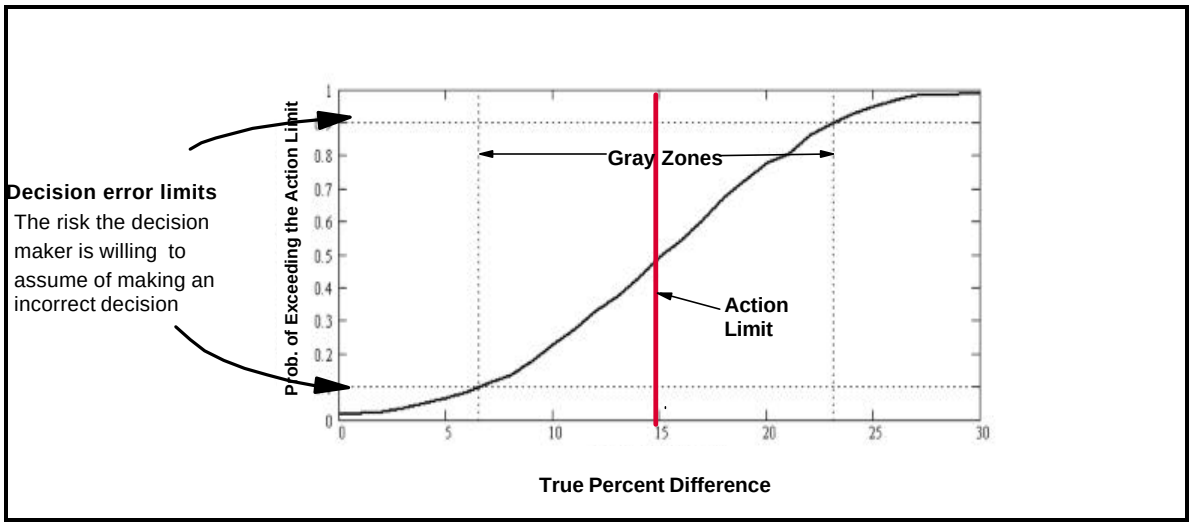

Figure 3.1 Example performance curve

Action limit - The action limit is the concentration or value that causes a decision maker to choose one of the alternative actions (e.g. a true 15% difference).

Performance curve - Is the model of the data based upon the input parameters associated with population and measurment uncertainties. The line itself is the true unknown concentration.

Gray Zone - The gray zone is the area between the performance curve(s) where the decision error rates are large but considered tolerable. These are tolerated because the high cost or resources required to "tighten" the gray zone outweigh the consequences of choosing the wrong course of action.

Decision Error Limits - These limits are established by the decision makers and presents the decision makers "comfort" with making a decision error, in the sense that a different decision would have been made if the decision maker had access to "perfect data" or absolute truth. The decision error limit in this example is 10%.

Power - This is the Y axis and represents the probability of deciding that the parameter concentration (on the performance curve) exceeds the action limit.

From Figure 3.1 the following statements could be made:

1. If one uses the performance curve on the right of the action limit one could say that a true difference between two consecutive three year means of 23% has a 90% probabilty of being declared as having a difference greater than 15%.

2. If one uses the performance curve on the left of the action limit one could say that a true difference between two consecutive three year means of 6% has a 10% probabilty of being declared as having a difference greater than 15%.

The performance curve is a powerful tool for illustrating what various uncertainties can do to the probability of making correct decisions. These uncertainties are used as input parameters that change the slope and width of the performance curves. Generally the "narrower" the gray zone and "steeper" the performance curve is, relative to the action limit, the higher the probability of making correct decisions. As an example, for the $PM_{2.5}$ program we have three sampling frequencies, every day, every 3 days, and every 6 days. As one increases sampling frequency from every six day to every day sampling, the gray zones narrows meaning that there is less probability for an incorrect decision with every day sampling (all other uncertainties being the same).

Simulation models were used to develop the NATTS data quality objectives. In determining the DQOs, no systematic sensitivity testing was conducted. An input parameter that

has strong sensitivities will change the gray zone more dramatically then a similar change to an input parameter that is less sensitive. Because the NAATS models are similar to the $PM_{2.5}$ model, the relative sensitivity to the various parameters was expected to be similar to what is known from experience with the $PM_{2.5}$ DQO model, with the exception of bias. No noticeable exceptions to this expectation were observed in the use of the model to establish the recommended DQO values. The expected relative sensitivities were:

- No sensitivity to a consistent multiplicative bias because of the numerical form of the estimate. A consistent bias will cancel out; the calculation produces the same answer regardless of the bias;
- Strong sensitivity to parameters controlling the number of samples, namely, the sampling frequency and the completeness for a given sampling frequency;
- Strong sensitivity to the population coefficient of variation (CV);
- Moderate sensitivity to the seasonality ratio;
- Relatively insensitive to changes in the measurement CV;
- Relatively insensitive to autocorrelation (one of the model parameters). We are assuming the "worst case" anyway;
- No sensitivity to the method detection limit (MDL) as long as the majority of the data are above the MDL. There is a very strong dependency on the MDL when the data are below the MDL; you cannot measure a trend when all of the data are below the MDL. The trends and hence the DQOs are based on a single pollutant at a time. "The majority of the data..." refers to a data set consisting of the concentration for a single species taken over a period of 6 years.

The technical approach used to develop DQOs followed the conceptual model developed for the $PM_{2.5}$ Federal Reference Method (FRM) DQOs. This conceptual model of simulating daily deviations from a seasonal curve was followed mainly due to its success in use with $PM_{2.5}$ and the flexibility of the conceptual model, which is a quite general model for simulating the characterization of ambient concentrations in terms of annual or multiyear averages from 1-in-n-day sampling. The model incorporates several sources of variability: seasonal variability, natural day-to-day variability, sampling incompleteness, and measurement error. The

measurement error was restricted to a precision component without a bias component, because the mathematical form of the assessment of trends is robust to multiplicative bias. Pollutant specific parameters were used in the modeling. The parameters describing the natural variation of the pollutants were based on data analyses of the pilot city data and EPA's air toxics data archive.

Input Parameters to the DQO Performance Curves

There are twelve input parameters used to develop the DQO performance curves. They were:

1. T1. This is the target decision error rate for when there is no change. It is always 10 percent.

2. T2. This is the target decision error rate for when there is a 30 percent decrease. It is always 10 percent.

3. The action limit. This is the minimum observed percent change from the mean concentration of the first three years to the mean concentration from the last three years that would be used to indicate that the concentrations have decreased. Decreases less than this amount would not be considered significant decreases in the mean concentration.

4. The sampling rate. It is set to one in six day sampling in each case.

5. The quarterly completeness criterion. This was set to 85 percent based on a review of the Pilot Study data completeness.

6. Measurement error Coefficient of Variation (CV). This was assumed to be 15 percent for each compound. (A sensitivity analysis showed that the DQOs are robust to moderate changes in this value.)

7. Seasonality ratio. This is a measure of the degree of seasonality. Specifically, it is the ratio of the highest point on the seasonal curve to the lowest point. A value of 1 indicates no

seasonality. Larger values make it more difficult to estimate an annual or three-year mean concentration, and hence larger values make it more difficult to measure the percent change.

8. Autocorrelation. This is a measurement of how quickly day-to-day deviation from the seasonal curve can occur. A value of 0 indicates that changes occur quickly enough that each day is independent of the preceding day. Values greater than 0 indicate that the changes are generally slower, so that days with concentrations above the seasonal curve are more likely to be followed by another day above the seasonal curve. Values greater than 0 increase the precision of the three-year means and the percent change between the three-year means. Hence, a value of 0 is the most conservative choice for the DQOs. Zero was used in all cases, because many daily measurements are required to obtain a reliable estimate of this parameter.

9. Population CV. This is a measurement of the natural variation about the seasonal curve. Larger values decrease the precision of the three-year mean concentration estimates and the percent change between them. The power curves are strongly dependent on this parameter, but the estimates can be strongly influenced by a few outlier values. Generally the 90^{th} percentile of the estimates from the Pilot study was used as a balance between these competing forces. This value was then rounded up to be a multiple of 5 percent for the urban DQOs. For the rural DQOs an additional 5 percent was added, since there were fewer rural sites on which to base the estimates.

10. MDL. This is the MDL used in the simulations. The value was chosen to be a reasonably attainable maximum for a site and compound.

11. Initial mean concentration. This is the mean concentration of the first three years in the simulations. Values closer to the MDL decrease the precision of the percent change estimate. The value chosen was approximately equal to the 25^{th} percentile of the site-compound means from the Pilot study.

12. Health Risk Standard. This value is shown for reference only. It was not used in the simulations.

Using these input parameters, performance curves were developed to try and determine what values for these parameters would be necessary to meet the initial DQO. Although the DQO is to determine a 15% difference between two consecutive 3-year periods, the DQO needs to be further refined to the statements below to include the decision error probabilities:

If there is no true decrease in the 3-year average concentrations, then the probability of observing a mean concentration for years four through six that is at least 15% below the observed mean concentration from years one through three should be no more than 10%.

If there is a true decrease in the 3-year average concentrations of at least 30%, then the probability of observing a mean concentration for years four through six that is less than 15% below the observed mean concentration from years one through three should be no more than 10%.

Equivalently, the second statement could read that:

If there is a true decrease in the 3-year average concentrations of at least 30%, then the probability of observing a mean concentration for years four through six that is at least 15% below the observed mean concentration from years one through three should be at least 90%.

The power curves shown in Appendix A demonstrate the probability of observing at least a 15% decrease as a function of the true decrease. In terms of the above goals this means that the power curve graphs should start below 10% for a true percent change of 0 and end above 90% for a true percent change of 30%. Since there is a particular interest in the error rates for no true change and for a true change of a 30% decrease, this associated x-axis (horizontal axis) range is shown for each curve. Also, it is sometimes useful to know when the two target error rates are

achieved. The range of "truth" between these values is referred to as the gray zone, i.e., the range of true percent decreases that cannot be reliably detected by the sampling scheme. These are also given for each curve (and indicated with vertical dotted lines).

In addition to the power curves, there are three sets of output values.

1. $Error_0$ is the percent of the model simulations with no change in the true three-year means that in fact generated at least a 15 percent decrease in the observed three-year means.

2. $Error_{30}$ is the percent of the simulations with a 30 percent decrease in the true three-year means that generated less than a 15 percent decrease in the observed three-year means.

3. The gray zone is the interval of the true decreases that cannot be detected with confidence by the study design. In this range, the probability of observing at least a 15 percent decrease is greater than 10 percent, but less than 90 percent.

A number of performance curves were run where the input parameters were varied while trying to meet the DQO requirements. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study, the specified air toxics trends DQOs will be met for monitoring sites that satisfy the goals of:

- **One in six day sampling frequency with at least an 85% quarterly completeness; and**
- **Measurement precision controlled to a CV of no more than 15%.**

Under these conditions, true decreasing trends of 30% or more can be detected at least 90% of the time between successive 3-year periods. Moreover, the error rate for when there is no true change between successive 3-year periods is controlled to be at most 10%. Sampling frequency and natural or environmental day-to-day variation are the primary factors affecting these error rates.

3.1.2 Explain the Use of Method Quality Objectives in the Absence of DQOs, and Provide a Clear Distinction between MQOs and Method Capabilities

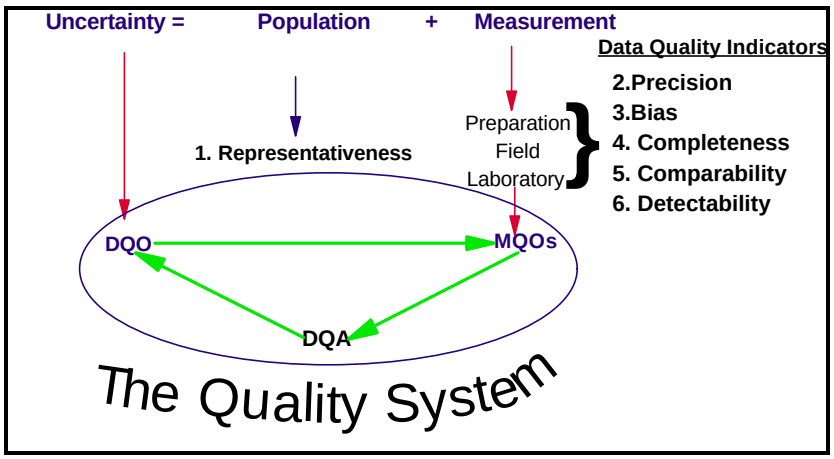

Figure ___ can be used to depict a quality system and where measurement quality objectives (MQO) fit into the process. Generally, MQOs are a product of the DQO process in that they provide the acceptable ranges for the data quality indicators identified in the figure. It is assumed that if one meets the MQO one would meet the DQO. Data quality assessmentd (DQA) are performed on the data quality indicators to determine whether in fact the DQOS were met. In the absence of DQOs a subjective decision is made as to acceptable ranges for the MQOs which upon some assessment, one could determine the uncertainty of the resultant monitoring data. Although the total uncertainty of the monitoring results depends on several factors that may not be under the control of the site, meeting MQOs or DQOs requires sites to meet the minimum quality specifications for monitoring methods presented in Section 4.

3.2 Monitoring and Quality Assurance Project Plan Elements

A QAPP must be developed by the monitoring organization (or their designee) for the NATTS Program. One QAPP can be used for multiple sites as long as all of the sites are operated under the same quality system. Every NATTS site must be included in the project QAPP for the monitoring organization. To keep key information in one document, the monitoring organization may combine other site-specific monitoring requirements into the NATTS project QAPP.

3.2.1 Why are a Monitoring Plan and a QAPP Important?

Implementation of a quality system on a project-specific basis involves development of a QAPP[2] to translate the DQO requirements into a specific action plan. Without this critical step in prior QA planning, the practical implications of meeting the DQOs will be lost in the daily operations of the project. Translating DQO requirements into a project-specific plan from the beginning is critical to the long-term success of the NATTS Program. The major components of the quality system are summarized in Figure 3.1-1. Implementation of the major components of a quality system for the NATTS project is accomplished by execution of a project-specific QAPP. Every site may have unique operation and logistical requirements, which must be considered in the project QAPP. The QAPP describes the project-specific procedures and process that must be implemented to meet the EPA global DQOs for NATTS Program and maintain consistency in the data developed from site-to-site across the national network.

3.2.2 How Specific Project Quality Objectives Would Complement DQOs for the NATTS Program

The sampling design and measurements methods selected in Step 3 of the DQO process must be sufficient to meet the acceptance criteria for decision making. Both the measurements confidence intervals and the number of data points (i.e., the frequency of collection episodes and the total number of episodes) must be used to develop a plan to meet the confidence required in the DQOs. To meet the minimum number of monitoring episodes for statistically significant trend analysis, NATTS Program monitoring locations must also remain in the same location for sufficient time (i.e., a minimum of three years). DQOs for NATTS include a minimum of 85% completion at the 1-in-6-day sampling frequency. Furthermore, **all sites** implementing these standardized measurements methods must meet the required analysis quality standards (e.g., method detection limits, initial calibration, periodic calibration quality checks) to ensure the national database for ambient air toxics is useful for national risk and trends analysis.

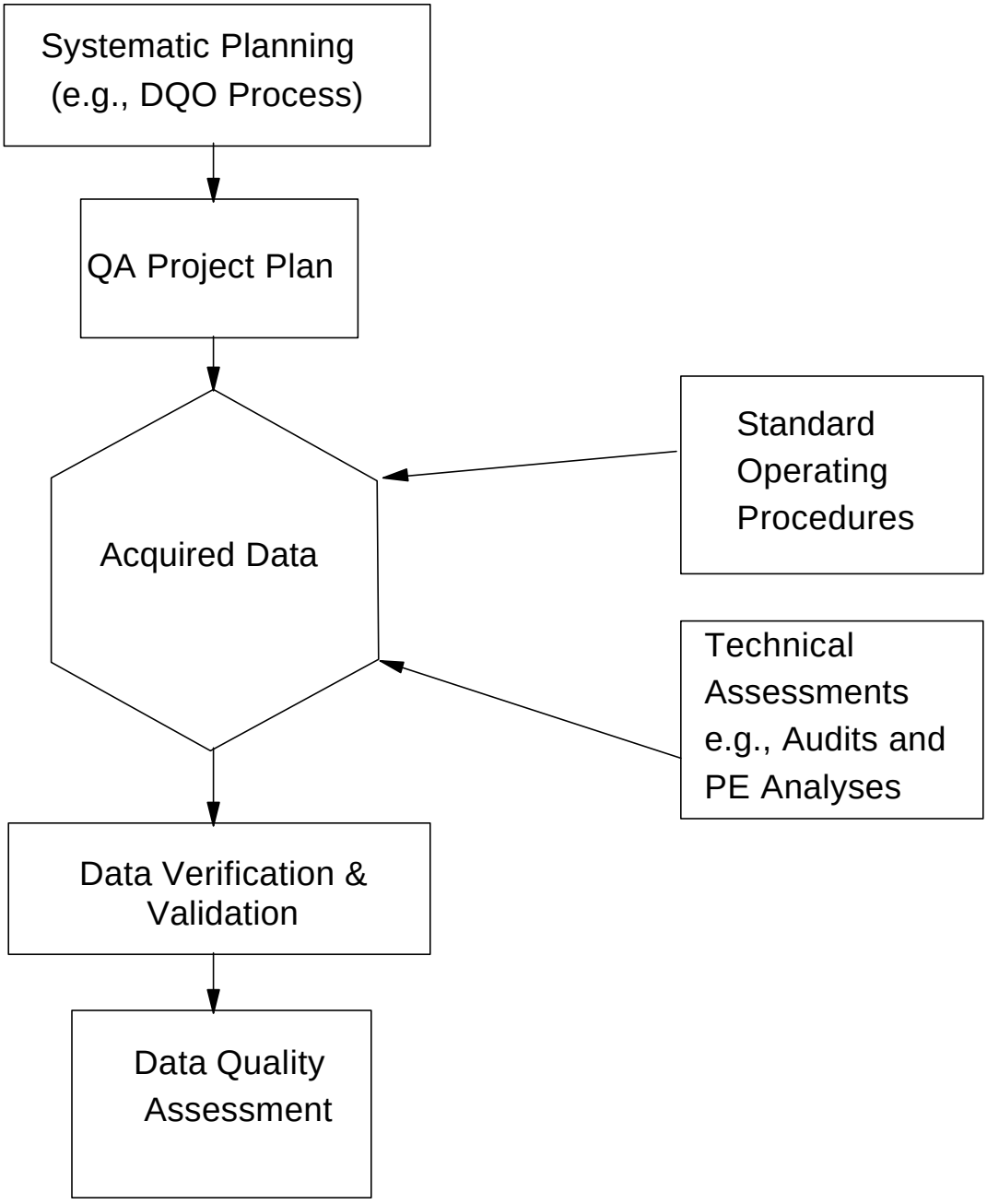
Systematic Planning
(e.g., DQO Process)
QA Project Plan
Acquired Data
Standard
Operating
Procedures
Technical
Assessments
e.g., Audits and
PE Analyses
Data Verification &
Validation
Data Quality
Assessment

Figure 3.1-1. General Quality System Components for NATTS Program

Selection and implementation of sampling and analytical methods are also important components of meeting the overall quality requirements for decisions about risk, air quality improvement, or cessation of monitoring. Individual NATTS Program monitoring locations must use the method approaches outlined in this TAD. The methods required for NATTS Program monitoring locations were selected based on historical experience and a comparison of minimum detection limits with health benchmarks. Substitution of a new or modified method for specific compounds can be done only after receiving EPA administrator approval, and the site management must demonstrate that the new method meets EPA's global DQOs for the NATTS Program.

3.2.3 NATTS Quality System Description

Program Description: EPA-Office of Air Quality Planning and Standards (OAQPS) plans to institute a quality system within the NATTS Program. The quality system will be integrated into the program via cooperation between the OAQPS, the Office of Research and Development (ORD), the EPA Regional Offices, the National Monitoring Program contractor, EPA Office of Radiation and Indoor Air (ORIA) and the state and local agencies. Each entity will have a vital role in the QA system. Below is a description of that system, discussed in detail in the NATTS Quality Management Plan[3] (draft) and the Implementation Plan and shown schematically in Figure 3.1-2.

State and Local Agencies: The state and local agencies have an important role in maintaining the **everyday quality**. With the help of OAQPS and the EPA regional offices, the state and local agencies will develop QAPPs prior to data collection. The QAPPs will be reviewed and accepted by the EPA regional offices. Once QAPPs are accepted, it is expected that the state and local agencies will adhere to the QA/QC procedures detailed in their QAPPs and associated standard operating procedures (SOPs). The QAPP must specify procedures for estimating **precision** of the sample collection methods (i.e., duplicate sample collection or collocated sample collection where additional sample collection equipment is available).

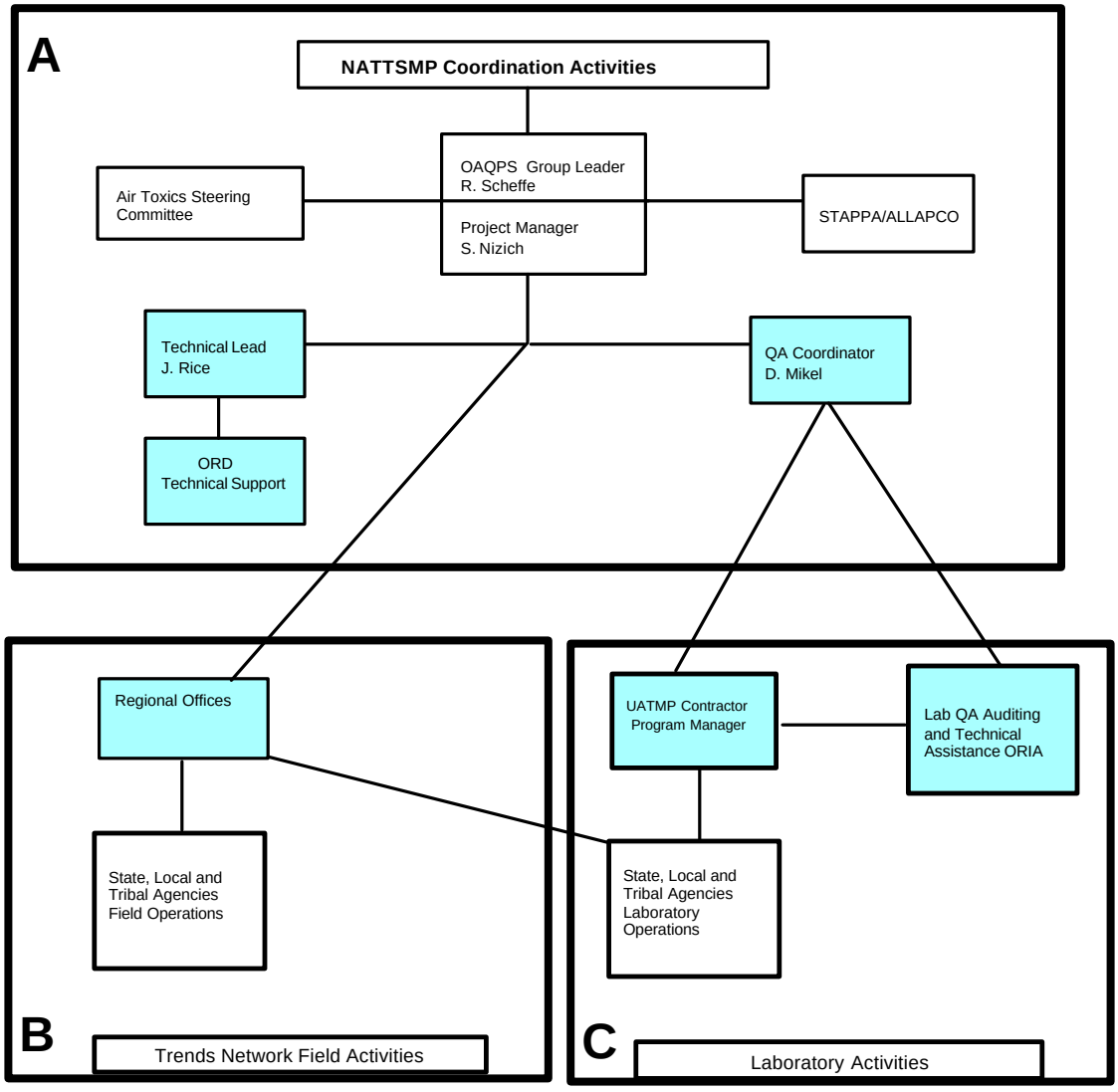

Figure 3.1-2. Operation of the NATTS Overall QA System

EPA Regional Offices: The EPA regional offices will be given the charge of reviewing and approving the QAPPs and SOPs. In addition, it is expected that the regional offices will perform performance evaluations (PEs) and technical systems audits (TSAs) on an annual basis. The TSA will focus on whether the state and local agencies are performing their operations according to the

accepted QAPP and SOPs. Data from the TSA will be used to estimate **compliance**. Data from the instrument performance audits (IPAs) will be used to estimate the **field accuracy** of the network. The regional offices will also perform **network reviews** for proper siting requirements. Results will be forwarded to OAQPS in the form of assessment reports.

National Monitoring Program Contractor: All NATTS monitoring locations will purchase a PE sample from the national monitoring program contract Section §105 funds at least quarterly. This sample will be "blind" and submitted to all state and local agencies' laboratories (subcontract laboratories as well). Results will be sent back to the national monitoring program contractor, who will forward this (assessment reports) information to OAQPS. These data will be used to estimate **laboratory accuracy**. Results will be forwarded to OAQPS in the form of assessment reports.

ORIA: Some of the agencies operating NATTS will use the national monitoring program contractor as their base laboratory. To provide external QA for the national monitoring program contractor, the ORIA laboratories in Montgomery, AL, and Las Vegas, NV, will provide PE samples and TSAs for the National Monitoring Program contractor. These data will provide **compliance** and **laboratory accuracy** for the National Monitoring Program contract. On OAQPS' request, ORIA may perform TSAs at state and local agency laboratories. In addition, ORIA will create "round-robin" samples that will be analyzed by all laboratories supporting the NATTS. These data will be utilized to estimate **laboratory bias**. Results will be forwarded to OAQPS in the form of assessment reports.

EPA-OAQPS: OAQPS has the responsibility to maintain the national QA program, so OAQPS will interact with each above-mentioned agency. Assessment reports will be forwarded to the EPA QA coordinator, who will create an **annual QA report** that will ascertain the uncertainty of the data. In addition, the EPA QA coordinator will work with all of the agencies

on issues of training, MDLs, data acceptance, validation and any other QA-related issues. OAQPS is developing **technical guidelines** for this program:

- A model QAPP that can be utilized by the state and local agencies to fulfill their requirement for a QAPP; available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/nattsqapp.pdf
- OAQPS is developing, through a contractor, a TAD to help the state and local agencies develop their SOPs; and
- OAQPS has developed, through a contractor, DQOs for a national network.

EPA-ORD: ORD has the responsibility to develop new field and laboratory analytical systems for the program.

3.2.4 How Specific Site Quality Objectives Would Complement Consistency between Sites in the NATTS Program

Each NATTS site must meet the quality requirements for site selection and measurement methods from this guidance. One goal of consistent application of quality objectives is to minimize the intersite variability of data. A complete QA/QC program requires consistent and persistent attention to evaluating the ongoing operation and quality of the performance of each part of the NATTS Program.

3.3 Hierarchy of QA Plan Levels

Project-specific QAPPs for NATTS Program monitoring locations must meet EPA requirements to generate data useable for assessment of trends. A monitoring site QAPP must address the 24 elements required by EPA for Category 1 environmental data collection operations. The purpose of each of the elements in EPA's QAPP requirement is described below. The following sections are consistent with EPA requirements in QA/R-5[2] and the model QAPP for the NATTS[3].

3.3.1 QA Project Plan Identification and Approval

The purpose of the approval sheet is to enable officials to document their approval of the QAPP. The title page and organization chart also identify the key project officials and their responsibilities for the work. The title and approval sheet should also indicate the date of the revision or the effective date of the plan and the document control number, if appropriate.

3.3.2 Table of Contents

The table of contents lists all the elements, references, and appendices contained in a QAPP, including a list of tables and a list of figures that are used in the text.

3.3.3 Distribution

QAPPs are controlled documents with restricted access: all the persons and document files designated to receive copies of the QAPP and any planned revisions should be listed in the QAPP. This list, together with the document control number, will help the project manager ensure that all key personnel in the implementation of the QAPP receive up-to-date copies of the plan and any subsequent revisions.

3.3.4 Project/Task Organization/Roles and Responsibilities

The purpose of the project/task organization element is to provide EPA and other involved parties with a clear understanding of the role that each party plays in the project, with the lines of authority and reporting for the project.

3.3.5 Problem Definition/Background

The background information places the problem in historical perspective and gives readers of the QAPP a sense of the project's purpose and position relative to other project and program phases and initiatives.

3.3.6 Project/Task Description

The project/task description provides an understanding of the project and the types of activities to be conducted, including the measurements to be taken and the associated QA/QC goals, procedures, and timetables for collecting the measurements: this element describes the work to be performed and the products to be produced.

- Sampling planned for the site. Description of sampling QA and how the site will be installed, operated and maintained.
- Measurements expected during the course of the project. Description of the measurement processes and techniques used to collect data. A brief description of analytical QA and how the laboratory analysis is conducted and checked is also included.
- Any special personnel and equipment requirements.
- Assessment techniques needed for the project. A discussion of the timing of each planned assessment and a brief outline of the roles of the different parties to be involved.
- A schedule for the work performed.
- Other descriptions needed. A description of data reduction, validation, and verification all the way to electronic database entry should also be included.

3.3.7 Quality Objectives and Criteria for Measurement Data

This element documents the quality objectives of the project and establishes performance specifications for the mandatory systematic planning process and measurement system that will be

employed to generate the data. The outputs from the DQOs process are used to develop this element.

3.3.8 Special Training Requirements/Certification

This element ensures that any specialized or unusual training requirements necessary to complete the project are known and furnished and the procedures are described in sufficient detail to ensure that specific training skills can be verified, documented, and updated as necessary.

3.3.9 Documentation and Records

This element defines which records are critical to the project and what information needs to be included in reports, as well as the data reporting format and the document control procedures to be used. The format of data reporting packages, whether for field or laboratory data, must be consistent with the requirements and procedures used for data validation and data assessment. The length of storage for the data reporting package may be governed by regulatory requirements, organizational policy, or contractual project requirements. This element of the QAPP should note the governing authority for storage of, access to, and final disposal of all records

3.3.10 Project Description

This element describes all the relevant components of the experimental design; defines the key parameters to be estimated; indicates the number and type of samples expected; and describes where, when, and how samples are to be taken, with anticipated start and completion dates for the project as well as anticipated dates of major milestones, such as the following:

- Schedule of sampling events;

- Schedule for analytical services by offsite laboratories;
- Schedule for phases of sequential sampling (or testing), if applicable;
- Schedule of test or trial runs; and
- Schedule for peer review activities.

If the purpose of the monitoring site is to track the trends in selected pollutants over a 3-year period, the characteristic (or parameter) of interest would be the difference between the mean concentration of the target compounds from year-to-year. This information is identified in Step 5 of the DQO Process. The relationship of this parameter to any decision that has to be made from the data collected is obtained from Steps 2 and 3 of the DQO Process.

The planning process usually recommends a specific data collection method (Step 7 of the DQO Process), but the effectiveness of this methodology rests firmly on assumptions made to establish the data collection design, such as the homogeneity of the air parcel to be sampled, the independence in the collection of individual samples (e.g., four separate samples rather than four aliquots derived from a single sample), and the stability of the conditions during sample collection (e.g., the effects of a rainstorm during collection of 24-hour air canister samples). The assumptions should have been considered during the DQO Process and should be summarized together with a contingency plan to account for exceptions to the proposed sampling plan. An important part of the contingency plan is documenting the procedures to be adopted in reporting deviations or anomalies observed after the data collection has been completed. Examples include an extreme lack of air parcel or sample homogeneity due to a temporary, unusual local source of a target analyte (e.g., local spill) or the presence of artifacts or components that interfere with analysis of target analytes (e.g., extreme high humidity) in the original sampling plan. Chapter 1 of EPA QA/G-9 provides an overview of sampling plans and the assumptions needed for their implementation, and EPA QA/G-5S[4] provides more detailed guidance on the construction of sampling plans to meet the requirements generated by the DQO Process.

All measurements should be classified as critical (i.e., required to achieve project objectives or limits on decision errors, Step 6 of the DQO Process) or noncritical (for

informational purposes only or needed to provide background information). Critical measurements will undergo closer scrutiny during the data gathering and review processes and will have first claim on limited budget resources. It is also possible to include the expected number of samples to be tested by each procedure and the acceptance criteria for QC checks.

If DQOs can be met with a nonstandard or modified method, EPA approval must be sought and secured before implementing the procedures on a routine basis. The purpose of the evaluation and approval process is to assess the potential impact on the representativeness of the data generated. This element of the QAPP should clearly reference any available validation study information.

3.3.11 Sampling Method Requirements

Environmental samples should reflect the target population and parameters of interest. As with all other considerations involving environmental measurements, sampling methods should be chosen with respect to the intended application of the data. Sampling methods for NATTS Program sites are described in Section 4. Sampling methods can materially affect the representativeness, comparability, bias, and precision of the final analytical result; therefore, EPA requires consistent application of these methods for the NATTS Program.

- Describe appropriate sampling methods. Appropriate sampling methods will be identified from guidance provided in this TAD. The QAPP should also specify the site-specific sample collection, storage, preservation and shipping procedures.

- Discuss sampling method requirements. Each medium or contaminant matrix has its own characteristics that define the method performance and the type of material to be sampled. Investigators should address the following:

  — Choice of sampling method; and

  — Preparation and handling of sampling media.

- Describe the precautions to avoid sample contamination. Contamination arises by handling of the sampling media or exposing of the sampling apparatus to a high

concentration of contaminants. All chemical measurements for the NATTS Program are directed at parts per billion (ppb)-level detection. Site-specific procedures must be written and performed to reduce or eliminate exposure of the media or sampling equipment to contamination, with procedures to prevent sample contamination (one-use sorbent cartridges, certified canister samplers), the protection of sampling media once samples have been collected to prevent contamination from outside sources, any temperature preservation requirements, and the permissible holding times to ensure against degradation of sample integrity. For example, procedures for storage and handling carbonyl sampling tubes should include instructions for use of gloves to protect the samples from formaldehyde arising from the operator's skin. Solvents of any type except high purity water should not be used in the NATTS Program since VOC samplers can easily be contaminated. Sorbent media for semivolatile HAPs should be stored under refrigeration before and after sample collection.

3.3.12 Sample Handling and Custody

This element of the QAPP should clearly describe all procedures that are necessary for ensuring that:

- Samples are collected, transferred, stored, and analyzed by authorized personnel;
- Sample integrity is maintained during all phases of sample handling and analyses; and
- An accurate written record is maintained of sample handling and treatment from the time of collection through laboratory procedures to disposal.

Proper sample custody minimizes accidents by assigning responsibility for all stages of sample handling and ensures that problems will be detected and documented if they occur. A sample is in custody if it is in actual physical possession or in a secured area that is restricted to authorized personnel. Sample custody procedures are necessary to prove that the sample data correspond to the sample collected. Sample custody procedures are completed by transfer of sample custody from field personnel to laboratory, sample custody within the analytical laboratory during sample preparation and analysis, and data storage.

3.3.13 Analytical Method Requirements

To maintain consistency throughout the NATTS Program, this TAD specifies the analytical methods to be used for this program. Analytical methods presented for use in the NATTS Program were selected based on performance criteria and the ability to meet program DQOs. Qualification requirements included detection and identification of target compounds at sub-ppb concentrations.

Each analytical laboratory should have complete stepwise sampling, analytical and/or sample preparation procedures documented in laboratory specific SOPs attached to the site-specific QAPP.

The QAPP should also address the issue of the quality of analytical data as indicated by the ability of the data to meet the method QC acceptance criteria. This section should describe what is done if the calibration check samples exceed the control limits due to mechanical failure of the instrumentation, if a drift in the calibration curve occurs, or if a reagent blank indicates contamination. This section should also indicate the authorities responsible for the quality of the data, the protocols for making changes and implementing corrective actions, and the methods for reporting the data and its limitations.

Preparation procedures should be described and standard methods cited and used as specified in Section 4 of this TAD. Detailed handling and preparation procedures are needed for samples collected on sorbent media such as carbonyl, semivolatile organic, and dioxin samples. Step-by-step SOPs[5] for the preparation of the project samples for analysis should be prepared and included in an appendix to the QAPP. The sampling containers, methods of preservation, holding times, holding conditions, number and types of all QA/QC samples to be collected, percent recovery, and names of the laboratories that will perform the analyses should be specifically referenced.

The citation of an analytical method may not always be sufficient to fully characterize a method because the analysis of a sample may require deviation from a standard method and

selection from the range of options in the method. The SOP for each analytical method should be cited or attached to the QAPP, and all deviations or alternative selections should be detailed in the QAPP. The standard analytical methods selected for the NATTS Program are presented in Section 4. Analyte class, reporting units, analysis method, sampling media, precision of replicate samples, bias compared to PE or audit samples, completeness and instrument detection range are shown in Table 3.1-2. Laboratories should develop a full set of QC and acceptance criteria for calibration, and daily calibration checks, which should be archived with the data. Method-specific MDLs, as required for the NATTS Program, are presented in Section 4. Each laboratory must determine MDLs for target analytes on a yearly basis at a minimum.

Table 3.1-2. Summary of Quality Control Criteria for NATTS Laboratory Analysis

Analyte Class	Reporting Units	Analytical Method	Collection Medium	Precision of Replicate Samples (CV)	Bias[1]	Completeness
VOCs	ppbv	TO-15	Canister	20%	± 30%	>85%
Carbonyl Compounds	ppbv	TO-11A	DNPH Sorbent Tube	15%	± 20%	>85%
SVOCs	total µg	TO-13A and SW-846 M-8270	XAD-2® Sorbent Cartridge	20%	± 30%	>85%
2,3,7,8-TCDD dioxins/furans	pg/m^3	TO-9A	PUF	15%	± 20%	>85%
Heavy Metals	ng/m^3	IO-3.5	Quartz Filter	15%	± 20%	>85%

TO = *EPA Compendium for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd Ed. EPA/625/R-96/01a, July 1999.

IO = *EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*. EPA/625/R-96/01b, July 1999.

[1]At concentrations 10 times greater than the MDL.

3.3.14 Quality Control Requirements

QC is "the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer." QC is both preventive and corrective in establishing techniques to prevent the generation of unacceptable data, so the policy for corrective action should be outlined based on information developed in QAPP Element 7, "Quality Objectives and Criteria for Measurement Data," which establishes measurement performance criteria. Many of these QC checks produce measurement data used to compute statistical indicators of data quality. The formulas for calculating such data quality indicators (DQIs) should be provided or referenced in the text.

A QC checklist should be used to discuss the relation of QC to the overall project objectives with respect to:

- The frequency of the check and the point in the measurement process at which the check sample is introduced;
- The National Institute of Standards and Technology (NIST) traceability of the calibration gas for VOCs in canisters, dilute liquid standards for carbonyls and semivolatile organic compounds, and neat standards if used for other nonstandard compounds;
- The matrix of the check sample;
- The level or concentration of the analyte of interest;
- The actions to be taken in the event that a QC check identifies a failed or changed measurement system;
- The formulas used to estimate DQIs; and
- The procedures used to document QC results, including control charts maintained in the laboratory (i.e., in the Laboratory Information Management Systems (LIMS) or in a notebook).

QC criteria for NATTS laboratory analysis are summarized in Table 3.1-2.

QC check data will be used to determine that measurement performance is acceptable by establishing QC "warning" and "control" limits for the statistical data generated by the QC checks (see standard QC textbooks or refer to EPA QA/G-5T for operational details). Procedures for checking the method performance against the acceptance criteria and who takes what action to ensure corrective action is taken will be documented.

This section should describe what will be done if there are serious flaws in the implementation of the sampling methodology and how these flaws will be corrected. For example, if part of the complete set of samples is found to be void, how will replacement samples be obtained and how will these new samples be integrated into the total set of data?

3.3.15 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

This element of the QAPP discusses:

- The procedures used to verify that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels;
- How inspections and acceptance testing of environmental sampling and measurement systems and their components will be performed;
- How deficiencies are to be resolved, when reinspection will be performed, and how the effectiveness of the corrective action will be determined and documented; and
- How periodic preventive and corrective maintenance of measurement, test equipment, or other systems and their components affecting quality will be performed to ensure availability and satisfactory performance of the system.

3.3.16 Instrument/Equipment Calibration and Frequency

This element of the QAPP describes the calibration procedures for instrumental analytical methods and other measurement methods used in environmental measurements. It is necessary to distinguish between defining calibration as the checking of physical measurements against accepted standards and as determining the relationship (function) of the response versus the concentration. The American Chemical Society (ACS) limits the definition of the term *calibration* to the checking of physical measurements against accepted standards, and uses the term *standardization* to describe the determination of the response function.

3.3.17 Inspection/Acceptance for Supplies and Consumables

Supplies and consumables for NATTS cover a range of items from laboratory solvents to replacement brushes for site samplers. This section of the QAPP should describe how and by whom supplies and consumables are inspected and accepted for use in the project. Acceptance criteria for such supplies and consumables should be stated.

All supplies and consumables that may directly or indirectly affect the quality of the project or task should be clearly identified and documented. Typical examples include extraction solvents, calibration gases, calibration liquids, sorbent tubes, sorbent material, ozone (O_3) scrubbers, hoses, clamps, replacement parts, personnel protection equipment, and deionized water. For each item identified, the inspection or acceptance testing requirements or specifications (e.g., concentration, purity, activity, or source of procurement) in addition to any requirements for certificates of purity or analysis should be documented. The quality of supplies must be compared to the QAPP requirements upon receipt from the vendor. For example, pesticide or chromatographic grade solvents are required for analysis, and technical grade solvents should be rejected.

Acceptance criteria must be consistent with overall project technical and quality criteria. If special requirements are needed for particular supplies or consumables, a clear agreement should be established with the supplier, including the methods used for evaluation and the provisions for settling disparities.

Procedures should be established to ensure that inspections or acceptance testing of supplies and consumables are adequately documented by permanent, dated, and signed records or logs that uniquely identify the critical supplies or consumables, the date received, the date tested, the date to be retested (if applicable), and the expiration date. These records should be maintained by the responsible individual(s).

3.3.18 Data Acquisition Requirements

This element of the QAPP should clearly identify the intended sources of data and other information that will be used in the project. Much of the data used for key decisions in the DQO process has been screened to ensure it meets NATTS Program criteria such as:

- Representativeness. Were the data collected to make preliminary decisions about site location from a population that is sufficiently similar to the population of interest and the population boundaries? How will potentially confounding effects (e.g., season, time of day, and air parcel type) be addressed so that these effects do not unduly alter the summary information?

- Bias. Are there characteristics of the data set that would shift the conclusions? For example, has bias in analysis results been documented? Is there sufficient information to estimate and correct bias?

- Precision. How is the spread in the results estimated? Does the estimate of variability indicate that it is sufficiently small to meet the objectives of this project?

- Qualifiers. Are the data evaluated in a manner that permits logical decisions on whether or not the data are applicable to the current project? Is the system of qualifying or flagging data adequately documented to allow the combination of data sets?

- Summarization. Is the data summarization process clear and sufficiently consistent with the goals of this project?

Information that is nonrepresentative (i.e., information that does not meet DQO or NATTS quality requirements) and possibly biased may lead to decision errors. Meteorological and exposure or inventory data used to identify potential NATTS monitoring locations should be checked for representativeness and bias. Pilot study data used to confirm the location of a site should be reviewed carefully to ensure that data meet the quality requirements for the long-term NATTS activity. Ideally, observations and transformation equations are available so that assumptions can be evaluated against the objectives of the project. This element should also include a discussion on limitations on the use of the data and the nature of the uncertainty of the data.

3.3.19 Data Management

This element should present an overview of the documentation trail generated by each sample collected by NATTS, including all mathematical operations and analyses performed on raw ("as-collected") data to change their form of expression, location, quantity, or dimensionality. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage, and retrieval. A diagram that illustrates the source(s) of the data, the processing steps, the intermediate and final data files, and the reports produced may be helpful, particularly when there are multiple data sources and data files. Figure 3.1-3 shows a typical data management process. Any internal checks (including verification and validation checks) that will be used to ensure data quality during data encoding in the data entry process should be identified together with the mechanism for detailing and correcting recording errors. Examples of data entry forms and checklists should be included. The details of the process of data acquisition from instrument files, data validation and comparison to prespecified criteria should be documented in the QAPP.

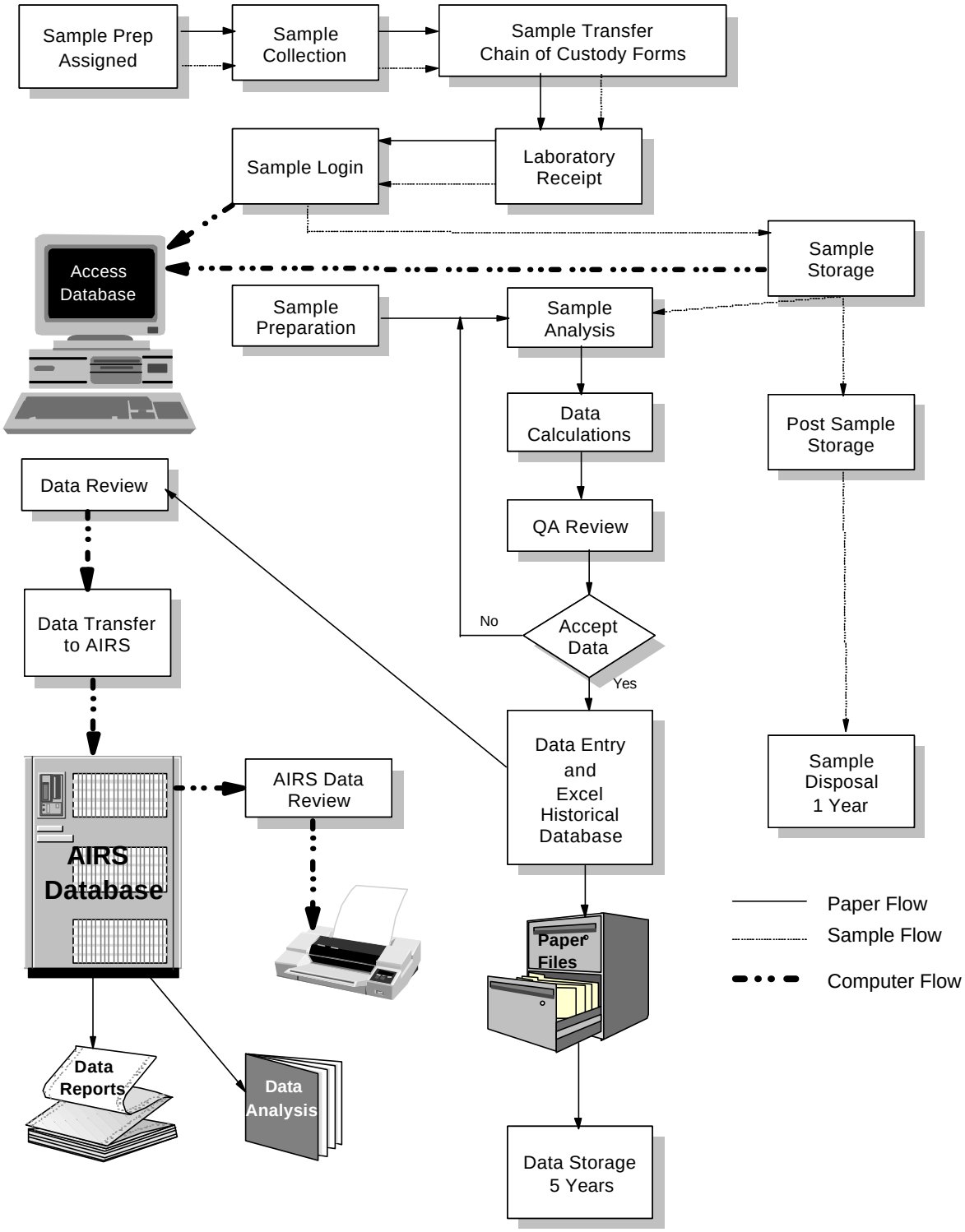

Figure 3.1-3. Example of Data Management and Sample Flow

These data management processes should include:

- Data transformation, or conversion of individual data point values into related values or possibly symbols using conversion formulas (e.g., units conversion or logarithmic conversion);
- Data transmittal, when data are transferred from one person or location to another or when data are copied from one form to another;
- Data reduction, including all processes that change the number of data items;
- Data analysis, involving comparing suitably reduced data with a conceptual model (e.g., a dispersion model); and
- Data management, including tracking the status of data as they are collected, transmitted, and processed.

The QAPP should discuss data storage and retrieval including security and time of retention and should document the complete control system. The QAPP should also discuss the performance requirements of the data processing system, including provisions for the batch processing schedule and the data storage facilities.

3.3.20 Assessments and Response Actions

During the planning process, sampling designs (EPA QA/G-5S, *Guidance on Sampling Design to Support QAPPs*[6]) have been chosen, including sample handling, sample preparation and analysis, and data reduction established based on standard method requirements and guidance in this TAD. To ensure that the data collection is conducted as planned, a process of evaluation of the collected data is necessary. This element of the QAPP describes the internal and external checks necessary to ensure that:

- All elements of the QAPP are correctly implemented as prescribed;
- The quality of the data generated by implementation of the QAPP is adequate; and

- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

Ongoing quality assurance should be implemented in layers. The top layer involves indicators of data quality like PE samples to generate an assessment of comparability and consistency. Round-robin or PE samples must be planned on a quarterly basis.

The second layer of QA is an independent internal review of data quality against established quality criteria. Review includes evaluation of duplicate and replicate measurement results, replicate laboratory analysis, ongoing precision and recovery data, control charts and internal calibration checks, and whether reported results meet acceptance criteria.

The third level of QA is the highest level of quality review—ensuring the SOPs for each of the sampling and analysis methods meet or exceed the bias and precision requirements necessary to meet the DQOs for the program. Site managers should periodically check the implementation of SOPs to ensure proper procedures are being followed. When staffing changes occur at a sampling site or in an analytical laboratory, cognizant mangers and QC staff must ensure new staff members are properly trained and certified for the work they perform and document this training.

Audits are formal assessments of program quality performed by an outside or independent QA organization.

- TSAs include a complete check of proper implementation of the QAPP. TSAs are performed at the beginning of a monitoring program to ensure all procedures and documentation are in place for program operation, with review of the documentation of the project, review of SOPs, auditing of field procedures (field audits) and laboratory procedures (laboratory audits). Throughout a TSA, emphasis is placed on implementation of the SOPs with particular attention to the adherence to QC requirements for sampling and analysis procedures. A TSA may be performed by EPA, an EPA contractor, or by the regional and state and local agencies themselves.

- PEs include submission of a PE sample for analysis by the supporting laboratory. EPA will provide quarterly PE materials for each of the standard analyses performed in the NATTS Program. Results of PE material analyses must meet the program

requirements. Corrective action must be taken and documented to bring analysis performance into compliance with program quality goals.

- DQAs[7] include review of the data reported in the NATTS Program from the initiation of sample collection through the reporting of the final results, often performed with an ongoing TSA to determine whether the original plan is being implemented according to design and whether the data management, review and final results are being generated correctly. A selection of calculations will be performed by hand at each stage of the data generation process. This assessment identifies not only failures in meeting data quality parameters but also general errors in calculation, transcription, and reporting. A DQA may be performed by EPA, an EPA contractor, or by the regional and state and local agencies themselves.

Internal assessments planned by each site should be described in the QAPP. The most important consideration is scheduling and documenting all planned internal assessments. Generally, internal assessments are initiated or performed by the internal QA Officer, so the activities described in this element of the QAPP should be related to the responsibilities of the QA Officer.

The following material describes what should be documented in a QAPP after consideration of the above issues and types of assessments:

- Number, frequency, and types of assessments. A schedule of the number of field audits, TSAs, PEs, and DQAs should be given. Assessments and informal audits may be performed by personnel internal to the project. At the initiation of monitoring site operation, a complete TSA should be performed by personnel external to the operation. Once data are being regularly generated by the monitoring site and support laboratory, a TSA combined with a DQA should be performed annually. Any other quality assessments required by state or local managers of the site should scheduled and described in this section of the QAPP. PE materials audits should be scheduled on a quarterly basis.

- Assessment personnel. The QAPP should specify the individuals, or at least the specific organizational units, who will perform the assessments. Internal audits are usually performed by personnel who work for the organization performing the project work but who are organizationally independent of the management of the project. External audits are performed by personnel of organizations not connected with the project but who are technically qualified and who understand the QA requirements of the project.

- Schedule of assessment activities. A schedule of audit activities, together with relevant criteria for assessment, should be given to the extent that it is known in advance of project activities.

- Resolution of issues. Audits, peer reviews, and other assessments often reveal findings of practice or procedure that do not conform to the written QAPP. Because these issues must be addressed in a timely manner, the protocol for resolving them should be given here together with the proposed actions to ensure that the corrective actions were performed effectively. The person to whom the concerns should be addressed, the decision-making hierarchy, the schedule and format for oral and written reports, and the responsibility for corrective action should all be discussed in this element, explicitly defining the unsatisfactory conditions upon which the assessors are authorized to act and listing the project personnel who should receive assessment reports.

3.3.21 Reports to Management

Effective communication among all personnel is an integral part of a quality system. Planned reports provide a structure for apprising management of the project schedule, the deviations from the approved QA plan, the impact of these deviations on data quality, and the potential uncertainties in decisions based on the data. Verbal communication on deviations from QA plans should be noted in summary form in the QAPP.

The QAPP should indicate the frequency, content, and distribution of the reports so that management may anticipate events and move to ameliorate potentially adverse results. An important benefit of the status reports is the opportunity to alert the management of data quality problems, propose viable solutions, and procure additional resources. If program assessment (including the evaluation of the technical systems, the measurement of performance, and the assessment of data) is not conducted on a continual basis, the integrity of the data generated in the program may not meet the quality requirements. These audit reports, submitted in a timely manner, will provide an opportunity to implement corrective actions when most appropriate.

3.3.22 Data Review

How closely a measurement represents the actual environment at a given time and location is a complex issue. (See *Guidance on Choosing a Sampling Design for Environmental Data Collection* (EPA QA/G-5S.[6]) Acceptable tolerances for each critical sample and the action to be taken if the tolerances are exceeded should be specified. The acceptance criteria for completeness, precision, and bias for NATTS are provided in Section 3. Local site management teams should develop sets of data review tools to ensure these criteria are met.

3.3.23 Data Review, Verification, and Validation Methods

The purpose of this element in the QAPP is to describe, in detail, the process used to validate (determine whether data satisfy defined user requirements) and verify (ensure that conclusions can be correctly drawn) project data. This element also includes methods for verification and validation. Acceptance or performance criteria are based on the ultimate use of the data to be collected and needed QA and QC practices required to support the final data use and decisions based on the data. In the decision-making process, these criteria allow a user to limit decision errors to a fixed level.

Data validation takes place at various stages in the development of final ambient air concentration data. Those responsible for field sampling must perform quality checks for the completeness of documentation from chain of custody (COC) through sample receipt and must periodically contact laboratory support staff to ensure valid samples are being collected and completeness goals are being met. Project managers must also coordinate the review of field data and laboratory data to ensure data are correlated with the correct samples. Laboratory data validation, including review, is primarily a function of the laboratory staff. The first stage of data validation occurs as data are generated by the bench chemist or analyst. QC checks including daily calibration samples, ongoing precision and recovery samples, system and field blank samples must all be reviewed as the data are generated. Laboratory staff should determine when

control measures indicate systems are out of acceptance specifications and make the necessary corrections as the samples are analyzed to facilitate reanalysis (if possible) of samples that do not meet quality requirements.

All of the laboratory data should be validated by a data reviewer prior to assembly of periodic reports of sample results. Final data review by laboratory quality staff should be done on a predetermined percentage of the data. The final evaluation and validation of the data must compare the QC results directly to the measurement quality objectives developed for the project. The percentage validated for the specific project together with its acceptance criteria should be outlined or referenced in the QAPP. Diagrams should be developed showing the various roles and responsibilities with respect to the flow of data as the project progresses. The QAPP should have a clear definition of what is implied by “verification” and “validation.”

Each sample should be verified to ensure that the procedures used to generate the data (as identified in the QAPP) were implemented as specified. Acceptance criteria should be developed for important components of the procedures, along with suitable codes for characterizing each sample's deviation from the procedure. Data validation activities should determine how seriously a sample deviated beyond the acceptable limit so that the potential effects of the deviation can be evaluated during DQA.

Once the data have been reviewed, verified and validated, the data should be loaded into a computer archive. This section of the QAPP must describe how the data will be analyzed in order to put the values collected into context with the NATTS data quality objectives.

3.3.24 Reconciliation with Data Quality Objectives

Reconciliation with DQOs can be performed where formal DQOs have been established. DQA is a key part of the assessment phase of the final data life cycle, as shown in Figure 3.1-3. As the part of the assessment phase that follows data validation and verification, DQA determines

how well the validated data can support their intended use. If an approach other than DQA has been selected, an outline of the proposed activities should be included.

Section 3: References and Resources

1. *Guidance for the Data Quality Objectives Process* (QA/G-4); EPA/600/R-96/055; U.S. Environmental Protection Agency, August 2000. Available at http://www.epa.gov/quality/qs-docs/g4-final.pdf.

2. *EPA Requirements for QA Project Plans* (QA/R-5), EPA/240/B-01/003; U.S. Environmental Protection Agency, March 2001. Available at http://www.epa.gov/quality/qs-docs/r5-final.pdf.

3. *Quality Assurance Guidance Document–Model Quality Assurance Project Plan for the National Air Toxics Trends Stations*; EPA 454/R-02-007; U.S. Environmental Protection Agency, December 2002. Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/nattsqapp.pdf

4. *Guidance on Quality Assurance Project Plans* (QA/G-5); EPA/600/R-98/018; U.S. Environmental Protection Agency, February 1998. Available at http://www.epa.gov/quality/qs-docs/g5-final.pdf .

5. *Guidance for the Preparation of Standard Operating Procedures for Quality-Related Documents* (QA/G-6); EPA/240/B-01/004; U.S. Environmental Protection Agency, March 2001. Available at http://www.epa.gov/quality/qs-docs/g6-final.pdf.

6. *Guidance on Choosing a Sampling Design for Environmental Data Collection* (QA/G-5S); EOA.240/R-02/005; U.S. Environmental Protection Agency, December 2002. Available at http://www.epa.gov/quality/gs-doc/g5s-final.pdf.

7. *Guidance for Data Quality Assessment*; EPA/600/R-96/084; U.S. Environmental Protection Agency, July 2000. Available at http://www.epa.gov/quality/qs-docs/g9-final.pdf

SECTION 4
MEASUREMENT METHODS FOR THE NATTS PROGRAM

4.0 INTRODUCTION

Section 4 presents information, guidelines, and specifications pertaining to the sample collection and analysis methods that will be applied to determination of the compounds of interest specifically for the NATTS Program. To accomplish consistency in the data generated across the entire nation, a standardized approach to conducting the methods presented below is mandatory. The information below presents specific configurations and approaches to accepted methods with the intent of standardizing sampling and analysis across the NATTS Program. This level of specification does remove flexibility but elevates consistency, a primary goal of the NATTS Program. NATTS participants wishing to use alternate configurations and/or approaches other than the procedures specified in this TAD may do so only with EPA approval; the NATTS participant must demonstrate equivalent performance to the methodology specified in this TAD prior to the initiation of sampling. The approval process is performance based, with the onus of proof of data consistency the responsibility of the applying agency. Details of this approval process are being developed.

4.1 OVERVIEW OF EPA COMPENDIUM METHOD TO-15

EPA Compendium Method TO-15[1] is the method used for sampling and analytical procedures for the measurement of subsets of the 97 VOCs that are included in the 188 HAPs listed in Title III of the Clean Air Act Amendments of 1990. These VOCs are defined as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25/C and 760 millimeters (mm) of mercury (Hg). This method addresses most conditions encountered in the sampling of ambient air into passivated canisters.

4.1.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities

The atmosphere is sampled by introduction of air into a specially prepared stainless steel canister. A sample of air is drawn through a sampling train comprising components that regulate the rate and duration of sampling into the preevacuated and passivated canister. After the air sample is collected, the canister valve is closed, the COC sheet is filled out and both are transported to the laboratory. Upon receipt, the canister arrival is recorded and the canister is stored until it is analyzed. Storage times of up to 30 days without significant compound concentration losses have been demonstrated for many of the VOCs.

To analyze the sample, a known volume is directed from the canister through a mass flow controller to a solid multisorbent concentrator. As a whole air sample, ambient humidity (i.e., water vapor) levels will be present. This water vapor can complicate the analysis processes. A portion of the water vapor will pass through the concentrator during sample concentration. The water vapor content of the concentrated sample can be reduced by dry purging the concentrator with dry helium. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The VOCs are then released from the trap by thermal desorption and swept by the carrier gas onto a gas chromatographic column for separation.

The analytical strategy for using Compendium TO-15 for NATTS Program analysis involves using a high resolution gas chromatograph (HRGC) coupled to a mass spectrometer (MS) operated by continuously scanning a wide range of mass to charge ratios (full SCAN mode). The fragmentation pattern from interaction of individual molecules with the MS ionization source (electron beam) is compared with stored spectra taken under similar conditions in order to calibrate for and identify the compounds. For any given compound, the intensity of the given fragment is compared with the system response to the given fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

4.1.2 Contamination

Canisters should be manufactured using high quality welding and cleaning techniques, and new or reconditioned canisters should be filled with humidified zero air and then analyzed after 24 hours to evaluate cleanliness. Although the 24-hour period is not a method requirement, new and reconditioned canisters have a higher potential for contamination due to the manufacturing processes, and it is therefore prudent to allow the humidified zero air to remain in the canister for a longer period to ensure that contaminants are desorbed from active sites. The cleaning apparatus, sampling system and analytical system should be assembled from clean, high quality components, and each system should be demonstrated to be free of contamination.

Impurities in the calibration, internal/tuning standard dilution and carrier gases, organic compounds outgassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing humidified zero air blanks. Nonchromatographic-grade stainless steel tubing, non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N® rubber components are potential contamination sources and must be avoided.

Significant contamination of the analytical equipment can occur whenever samples containing high levels of VOCs are analyzed, resulting in carryover contamination in subsequent analyses. Whenever a sample with high concentrations of VOCs is encountered, this sample should be followed by an analysis of humid zero air to check for carryover contamination.

4.1.3 Precision

Precision refers to the agreement between independent measurements performed according to identical protocols and procedures. Replicate analysis of duplicate samples is used to quantify "sampling and analytical precision specific to a single sampling system" (i.e., how precisely the sampling and analytical methods measure ambient air concentrations). A duplicate sample is a sample collected simultaneously with a primary sample (i.e., in two separate canisters through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the line from the sampler to each of the two canisters and doubling the flow rate applied to achieve integration over the 24-hour collection period. The difference between duplicate samples and collocated samples is that the duplicate samples are collected from two canisters using one collection system, whereas collocated samples are collected at the same time but using two completely separate collection systems. Replicate analysis of collocated samples is used to quantify precision between different sampling systems. Although collocated samples are highly desirable, the cost of an additional sampling system is usually prohibitive because collocated data would have to be acquired at every site. However, any NATTS site that is able should conduct both duplicate and collocated sampling.

Precision is a measurement of random errors associated with sampling and analysis of environmental samples. These errors may result from various factors but typically originate from random "noise" inherent to analytical instruments. Laboratories can easily evaluate analytical precision by comparing concentrations measured during replicate analysis of the same ambient air samples.

- Average concentration difference quantifies the difference between replicate analytical results for each compound. When interpreting central tendency estimates for the specific compounds sampled, central tendencies should be compared to the average concentration differences. If the average concentration difference of a compound exceeds or nearly equals its central tendency, the analytical method may not be capable of precisely characterizing annual concentrations. Therefore, data interpretations for these compounds should be made with caution.

- Relative percent difference (RPD) expresses average concentration differences relative to the average concentrations detected during replicate analyses. The RPD is calculated as follows:

$$RPD = \frac{\left|X_1 - X_2\right|}{\overline{X}} \times 100 \qquad (4.1\text{-}1)$$

Where:

X_1 = Ambient air concentration of a given compound measured in one sample;

X_2 = Concentration of the same compound measured during replicate analysis;

$\overline{X}$ = Arithmetic mean of X_1 and X_2.

Replicate analyses with low variability have lower RPDs (and better precision), whereas replicate analyses with high variability have higher RPDs (and poorer precision).

4.1.4 Sampling Procedure and Issues Associated with EPA Compendium Method TO-15

EPA Compendium Method TO-15[1] deals with sampling and analysis of VOCs—defined as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg (standard conditions). Sampling using the EPA Compendium Method TO-15 configuration and approach for NATTS entails integrated subambient pressure collection of these VOCs in precleaned, evacuated passivated stainless steel canisters (i.e., a whole air sample)[2].

4.1.4.1 Sample Inlet and Manifold

A sample inlet and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Glass sample inlet and manifold assemblies are commercially available. Alternatively, custom-made inlets and manifolds constructed of

chromatographic-grade stainless steel may be designed and fabricated. Examples of a typical glass sample probe and manifold assembly are presented below. If automated calibration techniques that periodically flood the manifold with calibration standards are to be applied for the criteria pollutants, a separate manifold would be required to support the VOC and carbonyl components of the NATTS Program network.

The sample inlet is constructed of glass that is approximately 1 in. o.d. The entrance of the sample inlet is configured with an inverted funnel approximately 4 in. o.d. The sample manifold is constructed of glass approximately 1.5 in. o.d. The manifold has ports for sample distribution; the number of ports must be equal to or greater than the total number of sampling systems to which sample will be delivered. To reduce the potential for bias, the port nearest to the entrance of the manifold should be reserved for VOC sampling.

Teflon bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken not to place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8- in. o.d. stainless steel tubing—tubing that is flexible and will accommodate the flow rates typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the inlet and manifold, and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is pulled through the sample inlet and manifold to reduce residence time and prevent back diffusion of room air into the manifold and to ensure that the sample air is representative of outside ambient air. Sample airflow through the sample inlet and manifold should be at least two times greater than the total airflow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample inlet and inlet funnel should be in the breathing zone at a height of approximately 2 - 4 meters (m) above ground level. In addition, the inlet funnel should be positioned more than 1 meter, both vertically and horizontally, away from the housing structure. The inlet funnel should be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the inlet funnel and any obstacle should be at least two times the height difference between the obstacle and the inlet funnel. Unrestricted airflow across the inlet funnel should occur within an arc of at least 270 degrees. The predominant and second most predominant wind directions must be included in this arc. If the inlet funnel is positioned on the side of a building, a 180-degree clearance is required. The glass inlet should be reinforced or supported along the straight vertical axis of the assembly. Typically, this support is provided by routing the inlet shaft through a rigid section of metal or plastic tubing secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 4.1-1 presents the manifold assembly in the vertical configuration. Figure 4.1-2 presents the manifold assembly in the horizontal configuration. If the horizontal configuration is used, the sample ports must point upward so material that may be present in the manifold will not be transferred into the sample lines.

With continuous use, the sample inlet and manifold can accumulate deposits of particulate material and other potential contaminants. The sample inlet and manifold should be cleaned to remove these materials at a recommended quarterly frequency. To clean the assembly, the sample lines and blower should be disconnected from the manifold. For safety, electric power to the blower should be terminated until the cleaning process is completed. The individual components are disassembled by disconnecting the inlet, manifold, collection bottle, and coupling devices from each other. The individual components should then be cleaned using heated, high purity distilled water (i.e., only high purity distilled water, no organic solvents or soaps) and a long-handled bottle brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling.

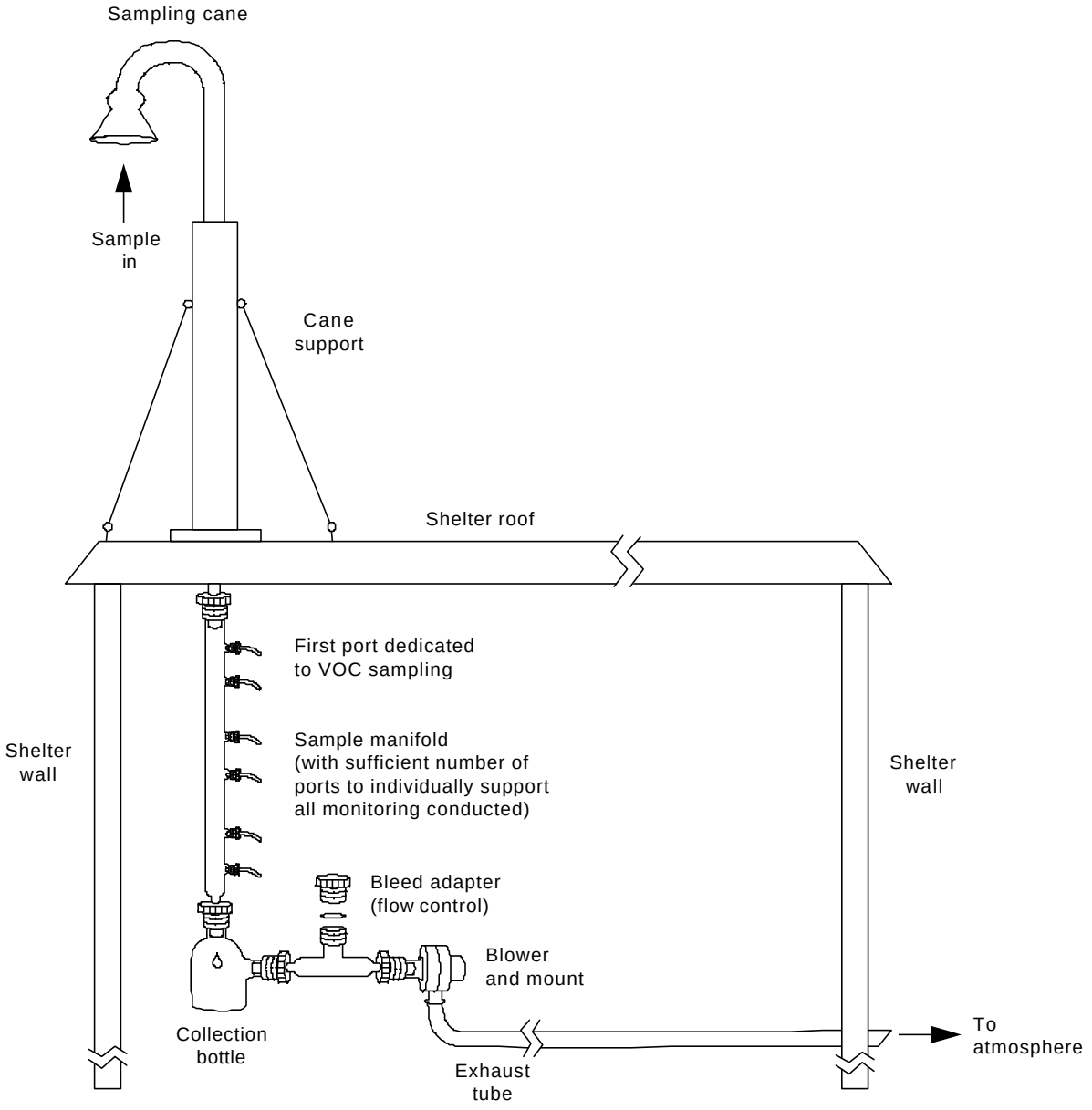

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Figure 4.1-1. Vertical Configuration

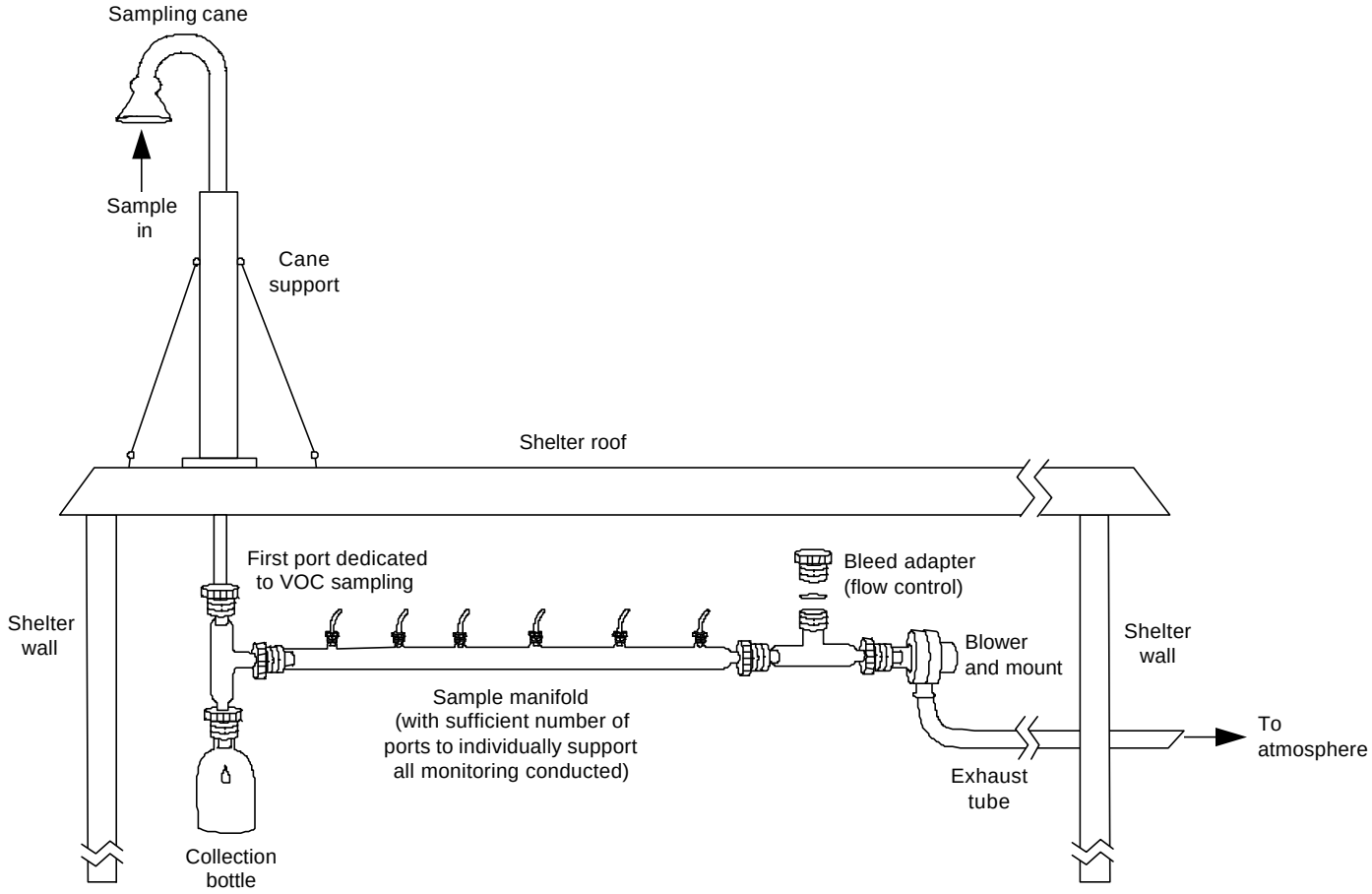

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Figure 4.1-2. Horizontal Configuration

4.1.4.2 Sampling Equipment

Canister samples are collected using a specific configuration of an automated sample collection system as presented in Section 4.1.5.3. Water vapor in the sample can condense on the canister surface under certain conditions and provide a sink for water-soluble compounds. One circumstance where this condensation can occur is when the canister is pressurized with sample air to levels above atmospheric pressure. In this case, water vapor accumulates in the canister until the partial pressure of the water exceeds the equilibrium vapor pressure at the canister temperature. To avoid losses of VOCs to condensed water in the canisters, the pressure of the air sample in the canister must not exceed atmospheric pressure. Under conditions of normal usage for sampling of ambient air to a subambient final pressure in canisters, most VOCs can be recovered from canisters near their original concentrations after storage times of at least 30 days.

Although EPA Compendium Method TO-15 makes provision for the collection of either negative or positive final pressure samples, because consistency of data is a paramount consideration for the NATTS Program, standardization on one approach is necessary. Canister sampling systems used to collect samples for the NATTS Program must meet the following specifications:

- The sampling system will yield a **subambient final sample pressure** (i.e., approximately 2 - 8 in. Hg).
- Integration of the sample collection will ideally be achieved using **electronic mass flow control**. Use of a critical orifice or vacuum regulator will be acceptable but considered a second choice. Sample sequencing, or collecting sample for only a portion of each hour, is not acceptable.
- The sample collection system will perform a **24-hour purge** with local ambient air before each sampling episode.
- The sampling system must incorporate either a latching solenoid valve or a solenoid valve with a **low temperature rise coil** (i.e., temperature rise of no more than 10°F when activated) to prevent excessive elevation of the sample gas temperature prior to collection.

- The sampling system will be configured so that the sample gas **does not pass through a pump** prior to collection in the canister.

Note that canister sampling systems can be made to be very complex. However, these complexities very frequently fail when the sampling system is required to operate for extended periods in the field without attendance. Consequently, sampling systems should remain as simple as possible and still accomplish representative integrated sample collection during the specified time period. A sampling system that will be used in the NATTS network is shown in Figure 4.1-3.

Canister sampling requires the collection and analysis of a large number of canister samples. The magnitude and success of the monitoring program depends on the quantity of canisters available, the capabilities and reliability of the sample collection system used and the availability and skill of field staff to address the sampling needs of the NATTS Program. Users of the canister sample collection methodology are responsible for the selection, setup and optimization of their systems and for the preparation of SOPs that delineate the details of all operations.

4.1.4.3 Components of the Specified Sampling System

The specified canister sample collection system consists of the following primary components:

- Inlet probe and manifold assembly. Constructed of glass or stainless steel. Used as a conduit to transport sample air from the atmosphere at the required sampling height and distribute sample air for collection by a variety of collection media.

- Bypass pump. A single- or double-headed diaphragm pump, or a caged rotary blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

- Sample inlet line. Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly.

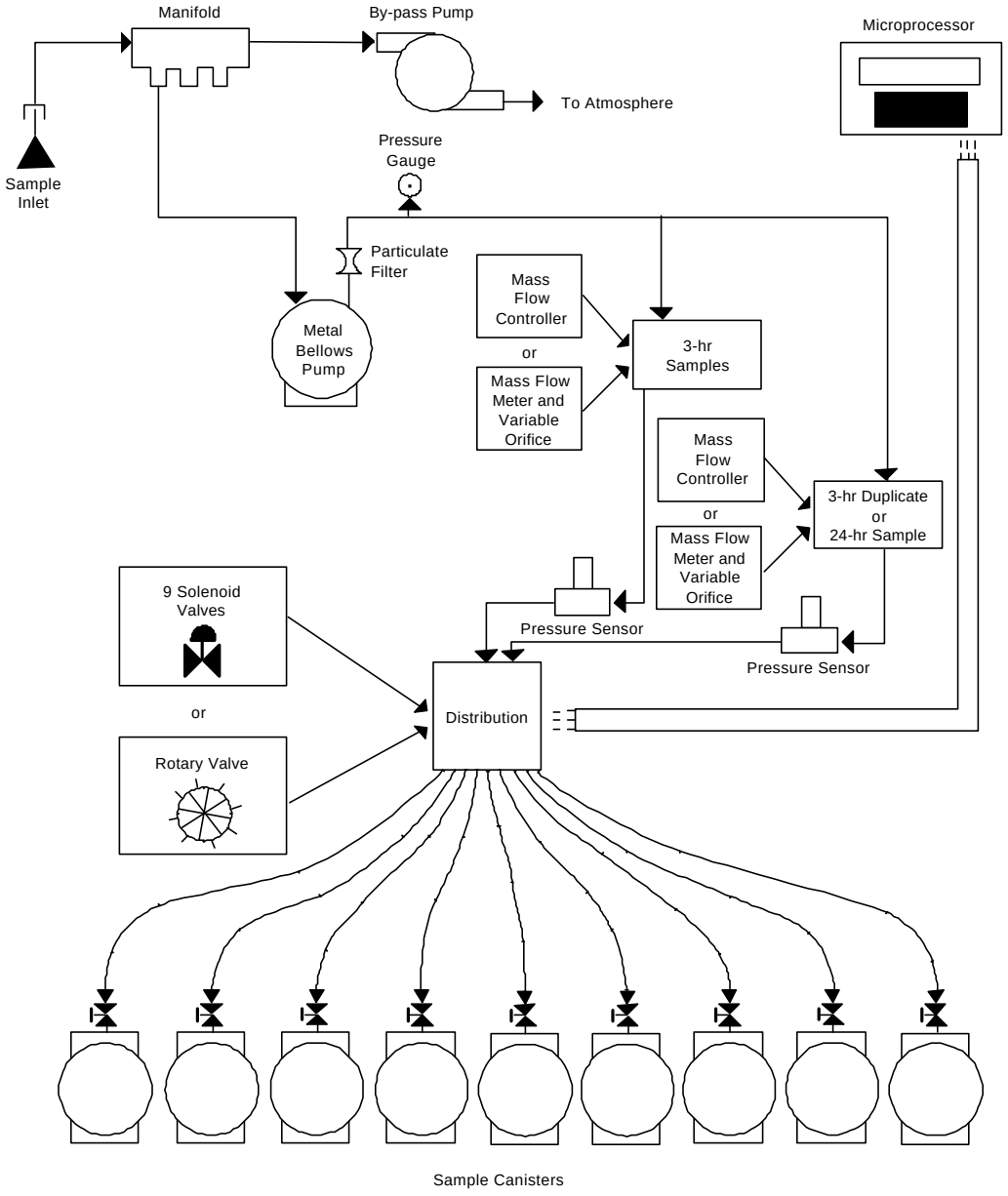


Figure. 4.1-3. A Typical Multiple-Event Sample Collection System

- Sample canisters. Passivated stainless steel sample vessels of desired internal volume with a bellows valve attached at the inlet of each unit. Used to contain the collected sample air for transportation and analysis.

- Stainless steel vacuum gauge (or optional electronic pressure sensor). A pressure measurement device capable of measuring vacuum (0 - 30 in. Hg). Used to measure initial and final sample canister pressures.

- Adjustable electronic mass flow controller . An indicating mass flow control device (or devices). Used to maintain a constant flow rate (±10%) over a specific sampling period under conditions of changing temperature (20 - 40°C) and humidity (0 - 100% relative).

- Particulate filter. Two-micron, sintered stainless steel in-line filter. Used to remove particulate material larger than 2 microns from the sample air being collected.

- Electronic timer (or optional microprocessor). An event control device. Used to allow unattended operation (activation and deactivation) of the collection system.

- Solenoid valve. An electric-pulse-operated or low temperature rise coil, stainless steel body, solenoid valve, with Viton® plunger seat and O-ring. Used to provide access to or isolation of the sample canister(s).

- Elapsed time indicator. A time measurement device used to measure the duration of the sampling episode.

- Stainless steel tubing and fittings. Isolation and interconnection hardware. Used to complete system interconnections. All tubing in contact with the sample prior to analysis should be chromatographic-grade stainless steel, and all fittings should be 316-grade stainless steel.

4.1.5 Canister Sampling System Certification

Canister sampling systems must exhibit nonbiasing characteristics before being used to collect samples. These sampling systems must be subjected to laboratory certification to quantify any additive or subtractive biases that may be attributed directly to the sampling system. The following procedure is required to certify canister sampling systems.

A challenge sample, consisting of a blend of organic compounds that span the analytical chromatographic range at a known concentration in clean, humidified zero air, is collected through the sampling system into a canister (over a 24-hour period). Typical challenge gas concentrations are approximately 10 parts per billion by volume (ppbv) per compound. A reference sample is concurrently collected using a dedicated electronic mass flow controller that has been characterized prior to each use. The samples are then analyzed using a gas chromatograph (GC) /MS system that is the primary analytical system used to analyze field samples or an alternate system that is equivalent to the primary system. The percent recoveries for target challenge compounds are calculated based on the concentrations determined for the reference sample. Recoveries of each of the challenge compounds should be in the range of 85 - 115% of the concentrations determined for the reference sample. A system-specific overall recovery should also be calculated. The overall recovery is the average of the individual compound recoveries. Each sampling system should have an overall recovery of 85 - 115%. The challenge sample percent recoveries are used to gauge potential additive and/or subtractive bias characteristics for each specific sampling system.

In addition to characterizing the sampling system with a blend of VOCs, the system should also be characterized using humidified zero air. A humidified zero air blank sample is collected through the sampling system to further gauge the potential for additive bias. The blank samples are analyzed for the specific NATTS Program VOC target analytes. The criterion applied to the blank portion of the certification process requires that the determined concentration for each target analyte species be 0.2 ppbv or less.

Sampling is accomplished using dedicated manifolds for both the zero and challenge phases of the certification procedure (Figures 4.1-4 and 4.1-5). Zero air supplied to the zero manifold should be hydrocarbon-free and humidified to approximately 70% relative humidity. The zero air should be supplied from a canister cleaning system similar to the one described below or an alternate system that is equivalent.

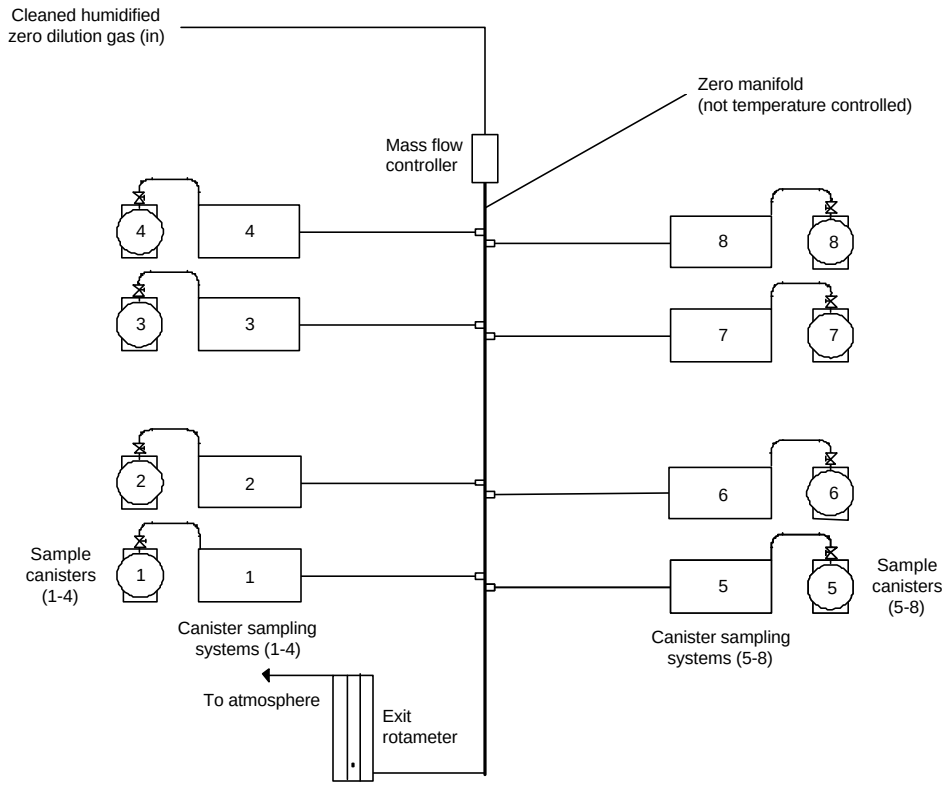


Figure 4.1-4. Dedicated Manifold for Zero Gas Certification

4.1.5.1 Certification Equipment

The equipment required to perform canister sampling system certification is described below. The equipment listed is consistent with the systems presented in Figures 4.1-4 and 4.1-5.

- Mass flow controllers. Mass flow controllers located at the inlets to the manifolds. Mass flow controllers are used to regulate the certification pollutant, diluent, and zero airflow rates.

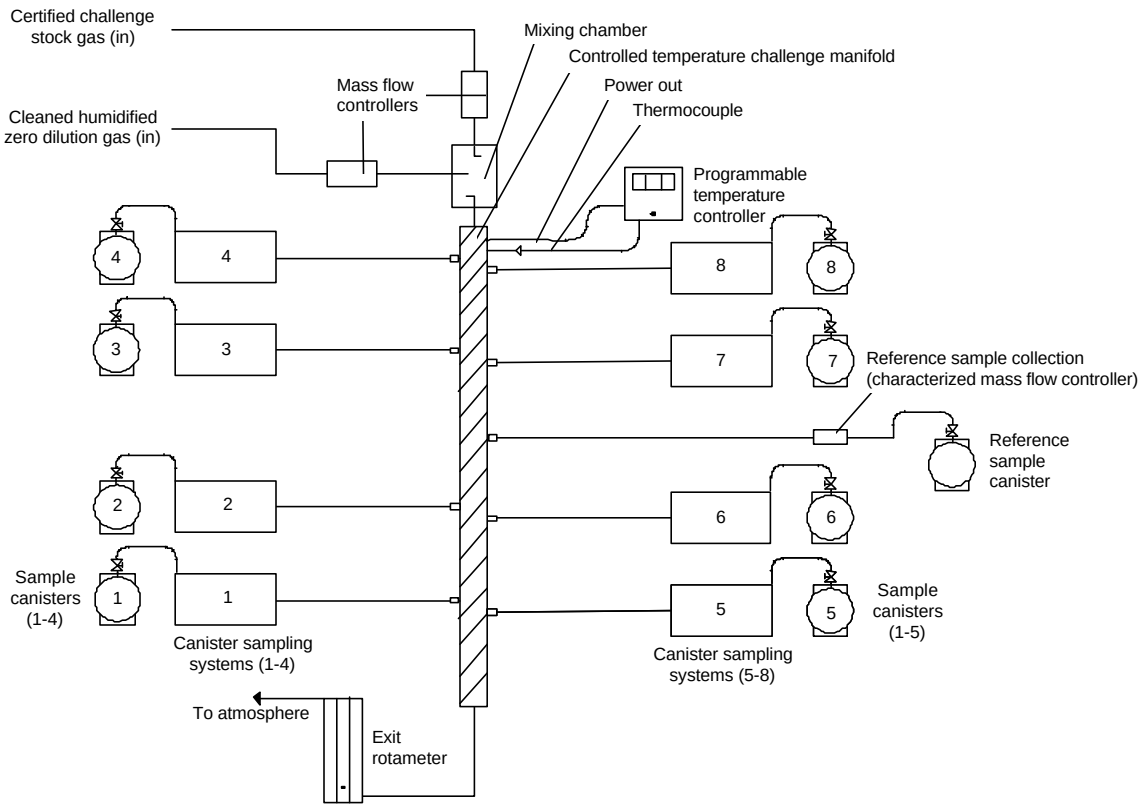


Figure 4.1-5. Dedicated Manifold for Challenge Gas Certification

- Zero air manifold. A zero air manifold (Figure 4.1-4) constructed of 1/4-in. o.d. chromatographic-grade stainless steel tubing and 1/4-in. fittings. The zero manifold is used to distribute zero air to the individual sampling systems being certified. The number of sample ports provided on the zero air manifold is determined by the number of sampling systems to be certified simultaneously.

- Exit rotameter. An exit rotameter located at the outlet of both the challenge gas and zero air manifolds. The exit rotameter is used to visually indicate that an excess of challenge gas or zero air is present in the respective manifolds during certification sample collection.

- Cord heater. A cord heater rated at 80 watts spiraled around the outside of the challenge manifold. The cord heater is used to heat the challenge manifold to 80°C. Heating the challenge manifold helps to reduce the potential for loss of challenge

gas compounds to the walls of the challenge manifold. The zero manifold is not heated.

- Temperature controller. A temperature controller used in conjunction with the cord heater to actively regulate the challenge manifold temperature at 80°C.

4.1.5.2 Certification Procedure

The procedure used to perform canister sampling system certification is presented below.

1. Perform a negative pressure leak check. Attach an evacuated canister to the exit of the sampling system. Open the canister bellows valve and record the initial vacuum, indicated by the sample pressure gauge. Close the canister bellows valve, view the sample pressure gauge and determine whether the vacuum is maintained (i.e., no change over a 10-minute (min) period). The system is leak free if the vacuum is maintained. If the vacuum is not maintained, the system is not leak free. Repair leaks and retest the system.

2. Connect the sampling systems and the reference sample flow controller to the zero manifold and purge them with humidified zero air for 48 hours. The purge air should simultaneously be routed to the challenge manifold to clean and prepare the challenge manifold for challenge sample collection. Terminate the humidified zero airflow at the end of the 48-hour period.

3. Purge the sampling systems, reference system, and manifold with dry zero air for 1 hour to remove accumulated moisture. During the dry purge, determine the certification flow requirements using the following equation:

$$Q_t = \left[(Q_s \times N_1) + (Q_R \times N_2)\right] \times F_1 \qquad (4.1\text{-}2)$$

Where:

Q_t = Total required flow rate (mL/min)

Q_s = Individual sampling system collection flow rate (mL/min)

N_1 = Number of sampling systems

Q_R = Reference system collection flow rate (mL/min)

N_2 = Number of reference systems

F_1 = Excess flow factor = 2.0

4. Determine the pollutant and diluent flows required to generate the desired concentration of challenge gas using the following equations:

$$F_2 = \frac{C_1}{C_2} \qquad (4.1\text{-}3)$$

Where:

F_2 = Dilution factor (for use in next equation)

C_1 = Desired challenge gas concentration (ppbv)

C_2 = Concentration of the stock cylinder (ppbv)

$$Q_P = F_2 \times Q_T \qquad (4.1\text{-}4)$$

Where:

Q_P = Pollutant flow rate (mL/min)

Q_T = Total required flow rate

$$Q_D = Q_T - Q_P \qquad (4.1\text{-}5)$$

Where:

Q_D = Diluent flow rate (mL/min)

5. Generate and deliver the challenge gas to the challenge manifold and sampling systems. Condition the challenge manifold with the challenge gas for 10 min with the sampling systems off. Condition the challenge manifold an additional 90 min with the sampling systems on and in the bypass mode. Connect a clean, evacuated canister to each sampling system.

6. Collect the challenge and reference samples. Conduct challenge sample collection according to the normal specified operation of the sampling system (for NATTS, 24-hour integrated collection at a flow rate that yields a subambient final pressure consistent with normal NATTS sampling).

7. Connect the sampling systems to the zero manifold and purge with zero air, humidified to 100% relative humidity, for 48 hours. Dry the manifold and samplers with dry zero air for 1 hour. Adjust the zero air stream to 70% relative humidity. Condition the zero manifold for 10 min with the sampling systems off. Condition the zero manifold an additional 10 min with the sampling systems on and in the bypass mode. Connect a clean, evacuated canister to each sampling system.

8. Collect the humidified zero air blank samples. Conduct the blank sample collections using the same sampling system operating procedures used during the challenge sample collection.

9. Analyze the zero and challenge samples and calculate the percent recoveries.

The sampling system must be challenged with a known concentration of selected analytes prior to deployment and annually thereafter. Operator/analyst judgment is critical: a challenge should be performed whenever the operation of the sampling system is questioned for any reason.

4.1.6 Canister Cleaning

The canister cleaning procedure and equipment described in this section are recommended when obtaining integrated whole ambient air samples for subsequent analysis of VOCs[3]. The cleaning procedure involves purging the canisters with cleaned humidified air and then subjecting them to high vacuum. The purpose of canister cleaning is to ensure that the interior canister surfaces are free of contaminants and that the canister meets the TO-15 cleanliness criteria (0.2 ppbv for all compounds of interest). This level of cleanliness minimizes the potential for carryover of organic pollutants from one sample to the next and helps to ensure that the samples collected are representative.

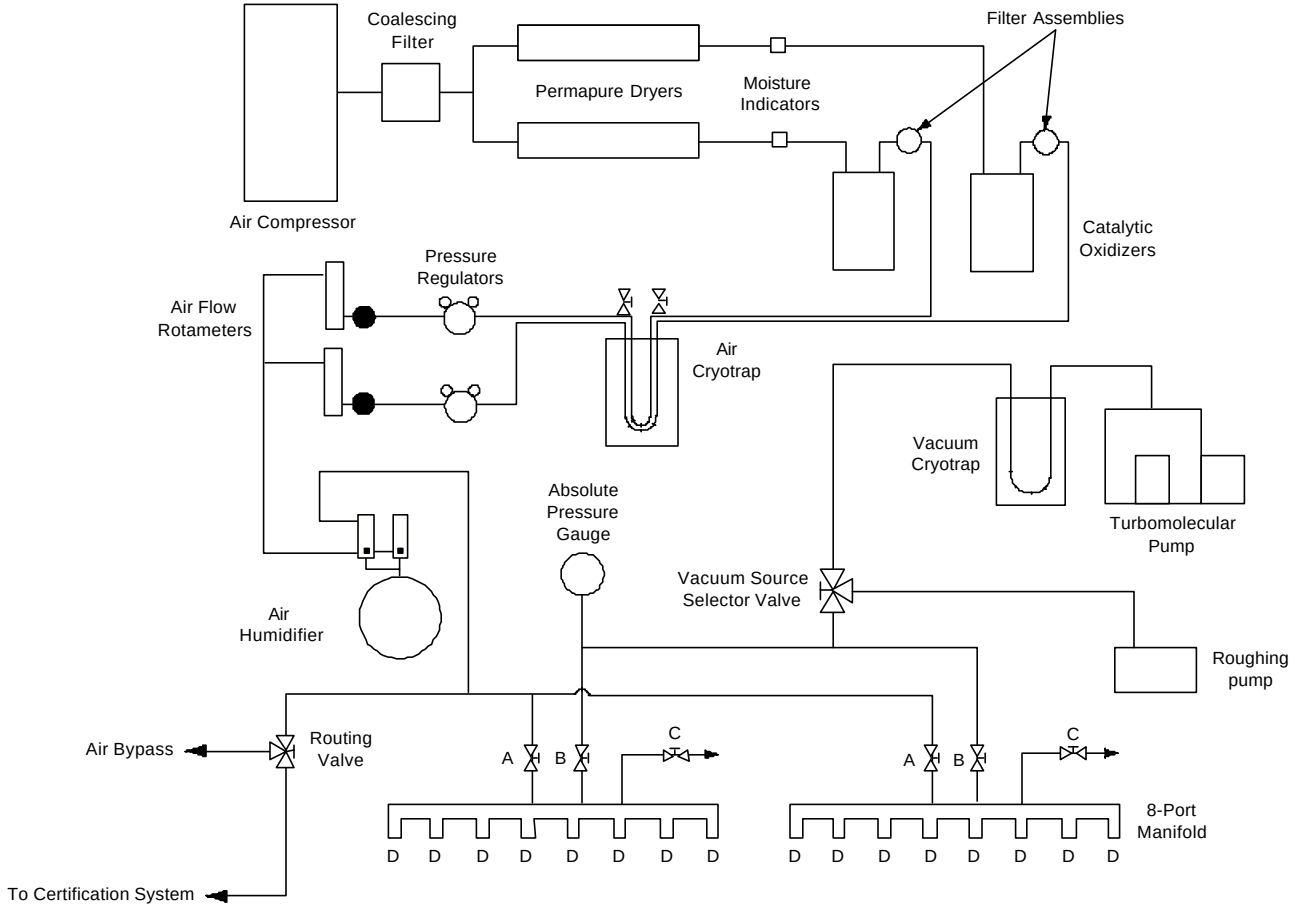
4.1.6.1 Canister Cleaning Equipment

The equipment required to clean canisters includes a source of clean, humidified air to pressurize the canisters to 20 pounds per square inch gauge (psig) and a vacuum system to evacuate the canisters to 5.0 mm Hg absolute pressure. Air from a standard, oil-free air

compressor will contain pollutants from the ambient air. In addition, various VOCs will be found in the compressed air because of the lubricants used in the air compressor. Canister sampling programs typically require the cleaning and preparation of large numbers of canisters. Consequently, an efficient cleanup system capable of handling large numbers of canisters is essential. Figure 4.1-6 presents the schematic of a canister cleanup system suitable for cleaning up to 16 canisters concurrently. This and any alternative system must include a vacuum pump capable of evacuating the canisters to an absolute pressure of 0.5 mm Hg. The equipment is designed so that one manifold of eight canisters is undergoing the pressurization portion of the cleaning cycle while the other manifold of eight canisters is undergoing the vacuum portion of the cleaning cycle.

The following equipment is incorporated in a typical canister cleaning system:

- Air compressor. A shop or laboratory oil-free air compressor used to provide the air supply for the canister cleanup apparatus.
- Coalescing filter. A coalescing filter designed to remove condensed moisture or hydrocarbon contaminants present in the air supplied from the air compressor.
- Permeation driers. Permeation driers used to dry the air prior to introduction into the catalytic oxidizers. Two permeation driers are installed in parallel. (Note: Chilled air moisture removal systems may be substituted for permeation driers.)
- Moisture indicators. Visual moisture indicators installed in the transfer lines between the permeation driers and the catalytic oxidizers to monitor the performance of the permeation drier.
- Catalytic oxidizers. Catalytic oxidizers installed in the clean-air system to oxidize any hydrocarbon contaminants that may be present in the air supplied by the air compressor. For best results and most efficient operation of the catalytic oxidizers, manufacturer's specifications should be strictly followed.



A. Manifold Air Pressure Valve
B. Manifold Vacuum Valve
C. Manifold Pressure Release Valve
D. Manifold Port for Connecting Canisters to be Cleaned

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Figure 4.1-6. Schematic of a Canister Cleanup System

- Filter assemblies. A 5-micron sintered stainless steel filter installed in the filter housing assembly downstream of each catalytic oxidizer to trap any particulate material that may be present in the airstream leaving the catalyst bed of the oxidizer.

- Air cryotrap and purge valves. The air cryotrap (i.e., liquid argon only) allows the cleaned air supply lines to be subjected to cryogenic temperatures to condense water formed during the oxidation of hydrocarbons, any remaining unoxidized hydrocarbons, and other condensables. Air cryotrap purge valves are used to purge these condensed components from the air cryotrap, as described in the operating procedure described below.

- Pressure regulators. A high purity, dual stage pressure regulator is installed in each branch of the air supply line so that the maximum pressure attained during the cleanup procedure is controlled at 20 psig.

- Flow controllers. The flow control devices shown in the canister cleanup schematic (Figure 4.1-6) are metering valves. The flow rates are set not to exceed the maximum recommended flow rate through the catalytic oxidizers.

- Airflow rotameters. Rotameters are installed in the air supply lines to allow monitoring of the flow rates through the catalytic oxidizers.

- Air humidifier. The air humidifier shown in Figure 4.1-6 is a passivated, double-valve stainless steel canister with an inlet dip tube that projects to the bottom of the sphere. High performance liquid chromatography (HPLC)-grade water is placed in the canister prior to use. Two rotameters are connected to control airflow so that about 80% of the flow rate can be directed to the humidifier (to bubble through the water to become saturated) while the other 20% bypasses the humidifier. This procedure allows the humidification apparatus to supply cleaned, dried air that has been humidified to a relative humidity of ~80%.

- Manifold air pressure valves. Manifold air pressure valves are used to isolate the air supply system from the manifold or to make the pressurized air available to the manifold.

- Eight-port manifolds. Eight-port manifolds are designed to allow up to eight canisters at a time to be connected. Fewer canisters may be connected to the manifold if the vacant ports are sealed off with a plug fitting.

- Roughing pump. The roughing pump shown in Figure 4.1-6 is a high capacity diaphragm vacuum pump used to remove the moist cleaning air from the canisters while evacuating the canisters to about 100 mm Hg absolute. The high moisture content of the cleaning air contained in the canisters will not impede the function of

this diaphragm-style pump but will impede the performance of the high vacuum pump

- High vacuum pump. A high vacuum pump capable of reducing the pressure in the canisters to 0.5 mm Hg absolute. High moisture content will impede the performance of the high vacuum pump.

- Vacuum cryotrap. A U-shaped trap located in the vacuum manifold that is sized to fit inside a Dewar flask filled with cryogen. The purpose of this trap is to condense water vapor from the air that is pulled from the canisters during the vacuum cycle and prevent back diffusion of organic vapors from the high vacuum pump into the canisters during the vacuum cycle of the cleaning procedure.

- Vacuum source selector valve. The vacuum source selector valve is a multi-position valve used to route either the roughing pump or the high vacuum pump to the eight-port manifold assemblies or to isolate both pumps from the manifold assemblies.

- Compound absolute pressure gauge. An absolute pressure gauge is used to measure the pressure attained in the canisters during the vacuum and pressurization cycles of the cleaning procedure. The absolute pressure gauge must be able to measure absolute pressures from 40 psig down to 0.5 mm Hg absolute.

- Air bypass valve. The air bypass valve is used to allow a 1.0-liter per minute (Lpm) flow of air to be maintained through the catalytic oxidizers when the cleaning system is not in use. This flow prevents the oxidizers from overheating when the cleaning system is not in use.

- Manifold valves. The manifold vacuum valve and the manifold pressure valve are used to apply vacuum or pressure to the canisters, as required during the cleaning procedure.
- Manifold ports. The manifold ports permit connection of the canisters to the manifold. Fittings that mate directly with the canister valve fittings are used. These connections will not leak during the pressurization portion or the vacuum portion of the cleaning procedure.

4.1.6.2 Canister Cleaning Procedure

The cleaning system is prepared for use by checking the position of all the valves. All valves should be closed initially with the exception of the air bypass valve. Both the air source and vacuum pump vacuum flasks should be filled with cryogen, and the high vacuum pump should

be actuated. These vacuum flasks must remain filled with cryogen throughout all cleanup activities. The inlet bellows valve on the humidifier is opened and the valve on the wet air rotameter is also opened. The valve on the dry air (bypass) rotameter should be closed to allow the air to become humidified. The system should stabilize for 10 min. After preparing the cleanup system, canister cleaning is performed using the following procedure.

1. Connect the canisters to be cleaned to the cleaning manifolds. Record the canister numbers and precleanup concentrations, if available, as determined by the last analysis, in the appropriate cleanup and canister history logbook. Record data pertinent to the vacuum and pressure cleanup cycles as they are completed.

2. Remove collected moisture from the air cryotraps by opening and immediately closing the air cryotrap purge valves. Removal of the collected moisture should be performed at the beginning of each pressure cycle so the cryotraps do not plug with ice.

3. Release pressure from the canisters by opening all the canister bellows valves and then opening the manifold pressure release valve. When venting is complete, leave the canister bellows valves open and close the manifold pressure release valve.

4. Begin the first vacuum cycle by actuating the roughing pump, placing the vacuum source selector valve in the roughing pump position, and opening the manifold vacuum valve.

5. Evacuate the canisters to approximately 100 mm Hg, as indicated by the absolute pressure gauge.

6. Position the vacuum source selector valve in the high vacuum pump position.

7. Evacuate the canisters to 0.5 mm Hg absolute pressure (or less) and maintain the vacuum for 30 min.

8. Close the manifold vacuum valve after the 30-min, high vacuum period has been completed.

9. Begin the first pressure cycle by purging the air cryotraps (refer to Step 2) and then closing the air bypass valve. Open the manifold air pressure valve. Using the airflow control valves, adjust the airflow rate to the manufacturer's recommended optimum flow rate for the oxidizers, as indicated by the air rotameters.

10. Check the pressure regulators to verify that they are set to deliver a final pressure of 20 psig. Fill the canisters to 20 psig. As the final pressure is attained, the flow rates indicated on the air rotameters will drop to zero regardless of the setting on the flow controllers because the pressure in the canisters and the pressure at the exit of the regulators reach equilibrium.

11. Close the manifold air pressure valve when filling is complete. Open the air bypass valve and adjust the airflow meters to 1.0 Lpm.

12. Release the pressure from the canisters after they have been under a 20-psig pressure for 30 min by opening the manifold pressure release valve.

13. Repeat Steps 4, 5, 6, 7, and 8 for Vacuum Cycle 2.

14. Repeat Steps 9, 10, 11, and 12 for Pressure Cycle 2.

15. Repeat Steps 4, 5, 6, 7, and 8 for Vacuum Cycle 3.

16. Repeat Steps 9, 10, and 11 for Pressure Cycle 3.

17. Close the bellows valves on all of the canisters.

4.1.6.3 Determination of Canister Cleanliness

Two methods are applied to determining the cleanliness of canisters prior to deployment for use in sample collection. EPA Compendium Method TO-12[3] is used to determine the total nonmethane organic compounds (NMOC) in ambient air using the preconcentration direct flame ionization detection (PDFID) with cryogenic preconcentration. The PDFID analysis[3] is used to verify canister cleanliness prior to sample collection. One canister out of each cleaned batch of canisters (i.e., one canister per eight cleaned) is analyzed by GC/PDFID following EPA Compendium Method TO-12[3] procedures and must contain less than or equal to 10 parts per billion by carbon (ppbC) NMOC. One canister out of every cleaned batch of canisters (i.e., one canister per eight cleaned) is analyzed by GC/MS following EPA Compendium Method TO-15[1] and must contain less than 0.2 ppbv of any NATTS Program target air toxics VOC. After the cleaned canister passes both of these tests, the whole batch of cleaned canisters associated with the analyzed canister can be prepared for sample collection. If the cleaned canister does not pass

both tests, the whole batch of canisters (eight) associated with the analyzed canister, including the analyzed canister, must be recleaned and checked again.

4.1.7 Sample Collection Procedure

A detailed SOP must be prepared for sample collection. A vacuum pump draws in ambient air from the sampling inlet and manifold assembly at a constant flow rate of approximately 100 cubic centimeter (cc)/min or greater. A mass flow control device is used to maintain a constant sample flow rate into the canister over a specific sampling period. Displacement of the vacuum in the canister with sample air is the mechanism that facilitates sample collection. The flow rate used is a function of the final desired sample pressure, the internal volume of the canister used, and the specified sampling period. A starting pressure of 5.0 mm Hg absolute for the canisters is assumed.

During operation, the timer is programmed to activate and deactivate the sample collection system at specified times that are consistent with the beginning and end of a sample collection period. The flow rate into the canister should remain constant over the entire sampling period.

Prior to field use, each sample collection system must be certified as nonbiasing. After the initial certification, samplers must be recertified on an annual basis. Sampler certification is discussed in Section 4.1.5. The canisters must also be demonstrated to be clean before each use. Canister cleaning is discussed in Section 4.1.6.

The following generic steps are provided for the operation of a sample collection system while collecting a single sample:

1. Activate the sample collection system and verify that the correct sample flow rate has been input into the mass flow controller. Allow the system to equilibrate for 2 min.

2. Deactivate the sample collection system and reset the elapsed time indicator to show no elapsed time.

3. Open the canister bellows valve.

4. Record the initial vacuum in the canister, as indicated by the sample collection system vacuum gauge, on the canister sampling field data sheet.

5. Record the time of day and elapsed time indicator reading on the canister sampling field data sheet.

6. Set the electronic timer to start and stop sampling at the appropriate times.

7. After sample collection, record the final sample pressure on the sampling field data sheet. Final sample pressure should be close to the desired calculated final pressure. Time of day and elapsed time indicator readings should also be recorded.

8. Close the canister bellows valve. Disconnect and remove the canister from the sample collection system.

9. Attach a field data form/airflow form to document the canister serial number, sample number, sample type, location, and collection date.

Calculation of method precision for the NATTS Program is determined by repeated analysis of duplicate samples. Consequently, 10% of all sample collections will be duplicate or collocated samples. A duplicate sample is a sample collected simultaneously with a primary sample (i.e., in two separate canisters through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the line from the sampler to each of the two canisters and doubling the flow rate applied to achieve integration over the 24-hour collection period. The difference between duplicate samples and collocated samples is that the duplicate samples are collected from two canisters using one collection system, whereas collocated samples are collected at the same time but using two completely separate collection systems. Although collocated samples are highly desirable, the cost of an additional sampling system is usually prohibitive because collocated data would have to be acquired at every site. However, any NATTS site that is able should conduct both duplicate and collocated sampling.

4.1.7.1 Specifications for the Sampling System

To ensure that the sample collection system meets the needs of the NATTS Program, the following system specifications should be presented to and addressed by the candidate vendor(s) prior to procurement:

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.

- The overall size of the sampling system should still be kept as compact as possible.

- The sampling system should meet all applicable electrical and safety codes, operate on standard 110-volt AC power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.

- The overall configuration, and the components comprising that configuration, should allow simple operation, maintenance, and service of the sample collection system, with the emphasis on simplicity. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. All surfaces that will come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton®. The use of Teflon or other plastics or polymers should be avoided because the absorption/desorption characteristics of these materials increase the potential for sample bias.

- The sample collection system must be certified as nonbiasing. The user must be able to document that the sample collection system design/configuration being considered can be or has been certified according to the prescribed procedures in Compendium Method TO-15[1], as described below.

- The sample collection system must be able to perform mass flow controlled time integration of the canister sample collections and allow for variable collection flow rates so canisters of different volume may be used.

- Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a canister sample collection system. Missed sample collections seriously impair the ability of the NATTS Program to meet DQOs. The user should specify that the vendor maintain an adequate supply of replacement parts and qualified service technicians to ensure that the absolute minimal number of sampling events is missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/components be delivered to the sampling site within two working days of order placement. The user should also specify that a sample collection system delivered to the vendor for repair or for other problems be serviced and returned to

the user expeditiously. A vendor's ability to meet these requirements should be a primary consideration in the selection of instrumentation.

4.1.8 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field canister samples[1,2].

4.1.8.1 Interferences

Interferences can confound the analysis by affecting the ability to identify the mass spectra, obtain accurate peak areas, or obtain an accurate retention time. Interferences can be introduced through the sample matrix, the sample canisters, the analytical system, or the canister cleaning system. In the case of a coeluting compound, the mass spectrum can still generally be interpreted unless the coeluting compound is an isomer of the compound of interest and the masses are the same or approximately the same. Very volatile compounds can display peak broadening and coelution with other species if the compounds are not delivered to the GC column in a very small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the GC column under subambient temperature conditions, mitigates this problem.

Sample moisture can lead to retention time shifts and poor peak shape; both retention time shifts and poor peak shape can result in peak misidentification. Carbon dioxide can be present as a large peak that causes retention shifts and loss of nearby smaller peaks; the presence of a large carbon dioxide peak can therefore result in peak misidentification. Moisture and carbon dioxide can be removed from the analytical system with the moisture management subsystem in the preconcentrator. The analysis of blanks will prove that the analytical system is free from interferences.

4.1.8.2 Chromatography Issues

The MS provides advantages over nonspecific systems using multiple detectors. These advantages include positive compound identification supported by spectral libraries, identification of nontarget compounds without the use of standards, and interpretation of coeluting compounds. An FID can be added to specifically quantitate a wide range of hydrocarbons at a high sensitivity.

Table 4.1-1 presents the VOCs analyzed by EPA Compendium Method TO-15[1], including the NATTS compounds. Acrolein is unpredictable and difficult to quantitate at low concentrations. The stability of this compound is affected by the type of sample canister used. In general, polar compounds, and to a lesser extent, nonaromatic compounds, do not consistently chromatograph well. Also, these compounds, especially the polar compounds, are not easily quantitated at low concentrations due to low detector response at the scan parameters mentioned in the Analytical Procedure section of this document.

4.1.8.3 Humidity

Humidity in canister samples can present some chromatography problems ranging from poor reproducibility to column degradation[4]. Some moisture from the sample invariably is delivered with the sample onto the chromatography column. This water is more easily tolerated by the analytical system when it is spread out over a longer time instead of injected all at once with the sample. Polar compounds have an affinity for water and can be difficult to

Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs

Compound	CAS#	Primary Ion	Secondary Ion
acetylene	74-86-2	26	25
propylene	115-07-1	41	39, 42
dichlorodifluoromethane	75-71-8	85	87, 101
chloromethane	74-87-3	50	52
dichlorotetrafluoroethane	1320-37-2	85	135, 87
vinyl chloride	75-01-4	62	64
1,3-butadiene	**106-99-0**	**54**	**53, 39**
bromomethane	74-83-9	94	96
chloroethane	75-00-3	64	66
acetonitrile	75-05-8	41	40
acetone	67-64-1	43	58
trichlorofluoromethane	75-69-4	101	103, 105
acrylonitrile	107-13-1	53	52
1,1-dichloroethene	75-35-4	96	98, 61
methylene chloride	75-09-2	84	49
trichlorotrifluoroethane	26523-64-8	101	151, 103
trans-1,2-dichloroethylene	56-60-5	96	98, 61
1,1-dichloroethane	75-34-3	63	65
methyl *tert*-butyl ether	1634-04-1	73	57
methyl ethyl ketone	78-93-3	43	72
chloroprene	126-99-8	53	88, 90
cis-1,2-dichloroethylene	56-60-5	96	61, 98
bromochloromethane	74-97-5	128	130, 49
chloroform	67-66-3	83	85
ethyl *tert*-butyl ether	637-92-3	59	87, 57
1,2-dichloroethane	107-06-2	62	64
1,1,1-trichloroethane	71-55-6	97	99, 61
benzene	**71-43-2**	**78**	**77**

(Continued)

Table 4.1-1. (Continued)

Compound	CAS#	Primary Ion	Secondary Ion
carbon tetrachloride	56-23-5	117	119
tert-amyl methyl ether	994-05-8	73	87
1,2-dichloropropane	78-87-5	63	62, 41
ethyl acrylate	140-88-5	55	99
bromodichloromethane	75-27-4	83	85, 129
trichloroethylene	79-01-6	130	132, 95
methyl methacrylate	80-62-6	41	69, 100
cis-1,3-dichloropropene	10061-01-5	75	39, 77
methyl isobutyl ketone	108-10-1	43	58, 100
trans-1,3-dichloropropene	10061-02-6	75	39, 77
1,1,2-trichloroethane	79-00–5	97	83, 61
toluene	108-88-3	91	92
dibromochloromethane	124-48-1	129	127, 131
1,2-dibromoethane	106-93-4	107	109
n-octane	111-65-9	85	57, 71
tetrachloroethylene	127-18-4	166	164, 131
chlorobenzene	108-90-7	112	77, 114
ethylbenzene	100-41-4	91	106
m-, *p*-xylene	108-38-3/106-42-3	91	106
bromoform	75-25-2	173	171, 175, 252
styrene	100-42-5	104	78, 103
1,1,2,2-tetrachloroethane	79-34-5	83	85
o-xylene	95-47-6	91	106
1,3,5-trimethylbenzene	108-67-8	105	120
1,2,4-trimethylbenzene	95-63-6	105	1220
m-dichlorobenzene	541-73-1	146	148, 111
chloromethylbenzene	100-44-7	91	126
p-dichlorobenzene	106-46-7	146	148, 111

(Continued)

Table 4.1-1. (Continued)

Compound	CAS#	Primary Ion	Secondary Ion
o-dichlorobenzene	95-50-1	146	148, 111
1,2,4-trichlorobenzene	120-82-1	180	182, 184
hexachloro-1,3-butadiene	87-68-3	225	227, 223

Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

chromatograph (i.e., peaks often become broad and/or tailing). The polar compounds may even shift retention times, depending on the delivery method of the moisture onto the column.

Reducing sample size can reduce the moisture that is collected and injected. Alternatively, an active moisture management subsystem can be incorporated in the preconcentrator to reduce moisture from the sample prior to injection onto the analytical system. Moisture removal should be done cautiously because some methods of removing water from the sample may also remove some of the compounds of interest, especially the polar compounds.

4.1.8.4 Equipment and Materials for VOC Analysis

The following equipment and materials are required for performing successful analysis of field canister samples[1,5].

- Automated preconcentrator and autosampler. This instrument is designed to interface between the sample contained in a canister and the chromatographic analytical system. A concentrator is used to concentrate the condensable (organic) portion of an air sample. The system is equipped with two traps, a hybrid 60/80 Tenax®/deactivated glass bead trap and a secondary Tenax® trap.

- GC/MS system. A gas chromatograph is an analytical system complete with a temperature-programmable gas chromatograph having subambient capabilities and with a DB-1 60 m x 0.32 mm, 1-micrometer (:m) film thickness fused silica capillary column or equivalent.

- MS. This instrument is capable of scanning from 23 - 350 atomic mass unit (amu) every 1 second or less. It uses 70 volts (nominal) of electron energy in the electron ionization mode and produces a mass spectrum that meets all criteria for the manufacturer's specifications for 4-bromofluorobenzene (BFB) tuning.

- Data acquisition and processing software. The data system software includes programs to calibrate and tune the MS, acquire data, and process data, as well as utilities for file management and editing. Tuning programs can adjust voltages in the ion source, calibrate mass assignments, and control the scanning of the mass analyzer. Data acquisition programs monitor the total ion current, automatically storing the mass spectra of GC peaks as they elute (scanning mode) or, alternatively, monitor the concentrations of particular ions (selected ion monitoring mode). The data system also includes a mass spectral reference library for identification of mass spectra.

- Calibration manifold. A dynamic flow dilution system can be assembled by the laboratory or obtained commercially.

- Calibration stock standard. The calibration stock/s should be traceable to an NIST standard reference material (SRM) and include the VOCs of interest in one or more cylinders.

- Laboratory control standard. The calibration stock(s) should be traceable to an NIST SRM and include VOCs to use as a second source standard daily calibration check. It does not have to include all of the VOCs of interest and can include other VOCs.

- Internal standards. These are commercially available or can be prepared by the laboratory with humidified air containing d_{14}-hexane, 1,4-difluorobenzene, and d_5-dichlorobenzene at a nominal concentration of 30 ppbv. The internal standard should be sampled directly from the vendor-supplied cylinder and not diluted.

- Tuning standard. A 30-ppbv BFB commercially available gas standard that can also be prepared by the laboratory by injecting neat liquid BFB into a cleaned and evacuated canister and filling with clean humidified air. The BFB standard can be prepared or purchased in the same cylinder as the internal standards gas mixture. Tuning criteria are shown in Table 4.1-2.

- Sample canisters. These canisters are stainless steel (typically 6 L internal volume), with valve and passivated inner lining (i.e., SUMMA® and Silco Steel®), available from a variety of manufacturers.

Table 4.1-2. 4-Bromofluorobenzene (BFB) Tuning Criteria

Target Mass	Relative to Mass	Lower Limit %	Upper Limit %
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

4.1.8.5 Analytical Procedure

Preparation of the Analytical Standards

Stock gas mixtures certified traceable to an NIST SRM are preferred. For the best economy, the stock gas mixtures should be about 500 ppbv per compound. Lower concentration stock standards can be used, but preparation/certification of lower concentration standards tends to cost more. The calibration standards are prepared by dynamic flow dilution of the stock gas with clean humidified air using a manifold and calibrated mass flow controllers. Although other methods can be used to prepare standards (i.e., syringe injection, pressure methods), the inherent reproducibility/accuracy of the alternative methods of standard preparation is not sufficient to meet requirements for data consistency. Humidified zero air is used as the diluent. The diluted stock gas is allowed to mix in the dilution system reservoir and is then introduced into a clean and evacuated canister. One standard canister should be prepared for each of the six calibration concentrations, 0.25 ppbv, 0.50 ppbv, 1.0 ppbv, 5.0 ppbv, 10.0 ppbv and 15.0 ppbv. Each standard must be assigned a unique standard identification number, and the preparation of each standard should be documented in the dilution system notebook. The prepared standards should be

allowed at least 24 hours to reach equilibrium prior to analysis. A diagram of a dynamic flow dilution system is included in Section 9.2 of EPA Compendium Method TO-15[1]. The mass flow controllers of the dilution system should be recalibrated annually, and the calibration should be documented in the dilution system notebook.

To calculate the final diluted compound concentration:

Diluted Conc. = (Original Conc.)(Stock gas flow rate)/(Airflow rate + Stock gas flow rate)

A certified cylinder (commercially available) of BFB and internal standards as a gaseous mixture should be attached to the preconcentrator system with stainless steel tubing. A 150-mL volume from a BFB/internal standard gas mixture in a cylinder is loaded through the preconcentrator system along with the sample to introduce the internal standards and BFB to the sample analysis. The same amount of the BFB/internal standard gas mixture is loaded with each analysis, whether sample, blank, or standard. Table 4.1-3 shows the internal standard compounds and their characteristic masses.

Table 4.1-3. Internal Standards and BFB: Characteristic Masses

Internal Standard Compounds	CAS No.	Primary Ion	Secondary Ion
d_{14}-hexane	21666-38-6	66	50, 100
1,4-difluorobenzene	540-36-3	114	63, 88
d_5-dichlorobenzene	2199-69-1	117	82, 54

Typical GC/MS Analytical System Operating Conditions

The information below provides a set of typical operating conditions for the GC/MS system in performing analysis of canister samples.

MS Information

Solvent Delay:	4.80 min
EM Absolute:	True
Resulting Voltage:	1800 (Usually set approximately 200 above the autotune)
[Scan Parameters]	
Scan Group:	1
Start Time:	4.80 min
Low Mass:	23
High Mass:	27
Threshold:	500
Sampling #:	4 (Resulting in 28 scans/second)
Scan Group:	2
Start time:	7.0 min
Low Mass:	32
High Mass:	43
Threshold:	500
Sampling #:	4
Scan Group:	3
Start Time:	8.00 min
Low Mass:	35
High Mass:	300
Threshold:	500
Sampling #:	4

Timed MS Detector Entries

Time (min):	44.00
State (MS on/off):	Off

GC Temperature Information

Column:	J&W DB-1, 60 m, 0.32 i.d., 1-:m film thickness
Injector Oven Temperature:	250/C
MS Transfer Temperature:	280/C
Oven Initial Temperature:	-50/C
Initial Time Temperature:	5.00 min

Level	Rate (/C/min)	Final Temp (/C)	Final Time (min)
1	15.00	0	0.00
2	5.00	150	0.00
3	25.00	275	5.20

Next Run Time: 48.53 min

Preconcentrator Interface Conditions

	Initial Temperature	DesorptionTemperature
Trap 1: Glass Bead/Tenax® Trap	-155/C	10/C
Trap 2: Tenax® Trap	-55/C	200/C
Cryofocuser	-185/C	100/C

	Volumes (mL)	Flow (mL/min)
Internal Standard	150	50
Sample	300	50
Final Flush	75	25
Trap1-Trap2 Transfer	40	10

4.1.8.6 Preparation of the GC/MS Analytical System

The analytical system must be characterized and optimized prior to operation. Such parameters as retention times, relative retention times, existence and identification (ID) of coeluting peaks, internal standard retention times, and method detection limits should be established prior to sample analysis.

The use of relative retention time (RRT) ID is incorporated in some data processing software and will compensate for any retention time variations. Separation of the internal standard from the target compounds must be achieved prior to analysis. The use of internal standards can help minimize the influence of analytical system variability.

To interface the preconcentrator system to the analytical system, megabore size (0.53 mm) stainless steel (Silco Steel®) tubing housed in a heated transfer line is used. The tubing is connected to the column at the injector port with a zero dead volume union. The column (helium) carrier flow is set to deliver about 1 mL/min (EPC @ 18 psi @ 100°C) to the MS. Flow from the

end of the column is verified before making the connection to the MS by inserting the end of the column into methanol and observing bubbles. After flow is verified, the end of the column is connnected to the MS with the MS transfer nut. The GC is allowed time to purge the ambient air from the instrument before the GC oven temperature is ramped above 100°C. The certified cylinder of BFB and internal standards gas mixture is attached to the preconcentrator system with stainless steel tubing to allow the BFB and the internal standards to be concentrated with the sample prior to injection. Any changes or maintenance to the system should be documented in a maintenance logbook dedicated to that system.

4.1.8.7 Initial Calibration

An initial multipoint calibration curve must be performed during setup of the analytical system and then once per quarter (three months), after any major instrument change, or if the daily acceptance criteria have not been met. The system must be recalibrated if the daily QC sample will not meet acceptance criteria. The calibration range is approximately 0.25, 0.5, 1, 5, 10, and 15 ppbv for each compound. The lowest calibration point, 0.25 ppbv, is intended to be near (but not at) experimentally determined MDLs at a level for which the standard can be prepared accurately and reproducibly. Each calibration standard must be analyzed once and the data processing software must be used to create a database with the calibration responses for all of the compounds and generate a complete response factor report that includes the percent relative standard deviation (RSD). The %RSD for each compound must be within ±30% with up to two compounds allowed to be within ±40%. The RRTs for each compound must be within 0.06 RRT units of the mean relative retention time (MRRT) for the compound. At the time of calibration, the analyst should record the expected due date (three months from the date of calibration) for the next calibration in the analysis logbook.

The relative response factor (RRF) is calculated as follows:

$$RRF = (A_t)(C_{is})/(A_{is})(C_t) \quad (4.1\text{-}6)$$

Where:

A_t = area count of the primary ion for the target compound to be measured

A_{is} = area count of the primary ion for the internal standard

C_t = concentration of the target compound (ppbv)

C_{is} = concentration of the internal standard (ppbv).

The RRTs are calculated as follows:

$$RRT = \frac{RT_t}{RT_{is}} \quad (4.1\text{-}7)$$

Where:

Rt_t = retention time for the target compound (seconds)

Rt_{is} = retention time for the internal standard (seconds).

The MRRTs are calculated as follows:

$$MRRT = \sum_{i=1}^{n} \frac{RRT}{n} \quad (4.1\text{-}8)$$

Where:

RRT = Relative retention time for each compound at each calibration level.

4.1.8.8 Analytical Sequence

Sample analysis can begin after the daily system performance check, continuing calibration (or initial calibration), laboratory control standard, and daily system blank criteria have met acceptance criteria. Daily quality control criteria are presented in Section 4.1.8.

- Instrument performance check (BFB tune). Use BFB to verify instrument tune at the beginning of each 24-hour GC/MS analysis time period to demonstrate that the tuning performance criteria have been met before any sample analyses. The mass spectral ion abundance criteria for the instrument performance check standard are shown in Table 4.1-2. If the criteria are not met, the MS must be retuned. Some MS software acquires the mass spectrum automatically and gives the user a pass or fail report. Alternately, the analyst should take the average spectrum of the entire peak and subtract the background spectrum at a point well away from the BFB peak.

- Daily calibration check standard. A mid-level calibration check standard must be analyzed daily before sample analysis to ensure that the initial calibration is still valid. A valid daily calibration must have a RPD for each response factor less than ±30% from the mean response factor of the initial calibration for all compounds. If the daily calibration is not valid, analysis of the calibration check sample should be repeated. If still not valid, system maintenance and/or recalibration with new standards is required.

$$RPD = \frac{RRF_t - MRRF_i}{MRRF_i} \times 100 \qquad (4.1\text{-}9)$$

Where:

RRF_t = RRF of the target compound in the daily calibration check.

$MRRF_i$ = mean RRF of the target compound in the most recent initial calibration.

A second source calibration check should be analyzed daily as a laboratory control standard (LCS). The second source gas mixture can be attached directly to the preconcentrator system if it is at a low concentration, such as 15.0 ppbv. The recoveries for the LCS should be

from 70% to 130% of expected concentration. If the daily LCS does not meet criteria, it should be reanalyzed. If still not valid, recalibration is required.

$$\% \text{ Recovery} = \frac{\text{observed value}}{\text{expected value}} \times 100 \qquad (4.1\text{-}10)$$

- Daily system blank. Analyze a zero air canister containing purified, humidified air after the calibration standard and before the samples to prove that the analytical system is clean. The acceptance criterion for a blank is <0.2 ppbv for any target compound or 3 times the detection limit of the compound, whichever is higher. If the system blank does not meet criteria, analysis must be repeated with a different zero air canister. If still not valid, the preconcentrator/GC/MS system must be checked for leaks and/or contamination. Canister cleaning batch blanks can be used for clean zero air blanks since one canister of each cleaned batch must be analyzed by GC/MS for the batch to be certified as clean.

4.1.8.9 Sample Tracking

Each sample canister received is recorded in the sample login notebook and assigned a unique laboratory identification number. The pressure of the canister is compared against the pressure recorded at the site to ensure the canister remained airtight during transport. If any leaks are detected, the sample is invalidated. The sample canister is then tagged with the laboratory identification number, site location, collection date, and canister pressure. The sample airflow COC is completed with the same information. Canister samples must be analyzed within 30 days of the sample collection date. If not, the data for that sample should be flagged.

4.1.8.10 Sample Analysis

Sample canisters are connected to the autosampler inlet ports and the canister valves are opened. While the GC oven is cooled to -50/C, the autosampler preconcentrator collects the specified volume of a single sample out of a canister along with the specified volume of the BFB/internal standard (IS) mixture and concentrates it in cryogenically cooled traps. The trapped

sample is then thermally desorbed onto the head of the subambient GC column, and the GC begins the temperature program. Each analysis should be recorded in the analysis logbook for that system, including such information as sample name, laboratory identification number, collection date, analysis date, analysis file name, calibration method used, can number, dilution factor, and volume of sample loaded.

The ISs for each analysis completed in the 24-hour GC/MS analysis period must be compared to those in the most recent calibration. The responses of each IS in the sample must be within ± 40% of the mean area response of those of the ISs in the multipoint calibration and the retention time of each IS must be within 0.06 min of the retention time of those in the calibration or the samples must be reanalyzed. If the area response for any IS changes by more than ± 40% between the sample and the most recent calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, a calibration check sample must be analyzed to determine whether the multipoint calibration is valid. If acceptance criteria are not met, recalibration is necessary. Reanalysis of samples analyzed while the GC/MS system was malfunctioning is necessary.

The ID of each compound in the sample must be verified by retention time and relative abundances of the primary and secondary ions. See Table 4.1-1 for characteristic masses. Each compound spectrum is compared against a reference spectrum from the spectral library. It may be helpful to subtract the background noise from the compound spectrum to aid in verification of that compound. A library search report can provide the tentative ID of nontarget compounds without the use of standards. Target compound concentrations in units of ppbv are calculated using the RRFs obtained in the initial calibration. The abundance of the primary ion is used for quantitation, unless there is an interference with the primary ion, then the secondary ion can be used. The calculation is shown below. After the data results have been verified and quantitated by the analyst, the data are reviewed by a second person, who verifies the compound IDs and quantitation and summarizes the data into spreadsheet tables. The tables are then reviewed by a third person to identify and investigate any apparent anomalies and to ensure that all calculations are correct. All analysis data and data reports are saved and archived electronically.

$$C_t = \frac{(A_t)(C_{is})(DF)}{(A_{is})(MRRF)} \qquad (4.1\text{-}11)$$

Where:

A_t = area count of the primary ion for the target compound to be measured

A_{is} = area count of the primary ion for the IS

C_t = concentration of the target compound (ppbv)

C_{is} = concentration of the internal standard (ppbv)

MRRF = mean RRF from initial calibration

DF = dilution factor. DF = 1, if no dilution.

4.1.8.11 Sample Dilution

Samples with analtye concentrations greater than the calibration range should be diluted either by reducing the 300 mL sample volume or (in the canister) by adding clean pressurized nitrogen or air. Samples diluted with nitrogen or air should be allowed 24 hours for equilibration before analysis. A dilution factor must be applied to the data for either a volume dilution or dilution by nitrogen or air. For samples loaded at a lower volume, the dilution factor can be calculated dividing the usual sample volume by the dilution sample volume.

4.1.9 Requirements for Demonstrating Method Acceptability for VOC Analysis

Three measurements of method acceptability are presented below.

4.1.9.1 Determination of Method Detection Limits

MDLs for the ambient air analysis are experimentally determined in accordance with 40 Code of Federal Regulations (CFR), Part 136, Appendix B, with 99% confidence level with a standard deviation estimate having n - 1 degrees of freedom. The VOC MDLs in Table 4.1-4 present the maximum acceptable MDLs allowable to ensure consistency across the NATTS Program. It is recognized and understood that the target MDLs shown in Table 4.1-4 are significantly lower than the MDLs reflected in Compendium Method TO-15[1].

Table 4.1-4. Method Detection Limits for GC/MS Analysis of VOCs[1]

Compound	MDL (ppbv)	Compound	MDL (ppbv)
acetylene	0.06	1,2-dichloropropane	0.07
propylene	0.05	ethyl acrylate	0.33
dichlorodifluoromethane	0.07	bromodichloromethane	0.06
chloromethane	0.09	trichloroethylene	0.10
dichlorotetrafluoroethane	0.06	methyl methacrylate	0.36
vinyl chloride	0.09	*cis*-1,3-dichloropropene	0.11
1,3-butadiene	**0.10**	methyl isobutyl ketone	0.22
bromomethane	0.11	*trans*-1,3-dichloropropene	0.11
chloroethane	0.13	1,1,2-trichloroethane	0.19
acetonitrile	0.46	toluene	0.08
trichlorofluoromethane	0.14	dibromochloromethane	0.10
acrylonitrile	0.52	1,2-dibromoethane	0.11
1,1-dichloroethene	0.10	octane	0.10
methylene chloride	0.06	tetrachloroethylene	0.06
trichlorotrifluoroethane	0.07	chlorobenzene	0.09
trans-1,2-dichloroethy-lene	0.07	ethylbenzene	0.11
1,1-dichloroethane	0.08	*m*-,*p*-xylene	0.13
methyl *tert*-butyl ether	0.23	bromoform	0.13

(Continued)

Table 4.1-4. (Continued)

Compound	MDL (ppbv)	Compound	MDL (ppbv)
methyl ethyl ketone	0.34	styrene	0.12
chloroprene	0.05	1,1,2,2-tetrachloroethane	0.19
cis-1,2-dichloroethylene	0.10	*o*-xylene	0.14
bromochloromethane	0.12	1,3,5-trimethylbenzene	0.11
chloroform	0.06	1,2,4-trimethylbenzene	0.12
ethyl *tert*-butyl ether	0.18	*m*-dichlorobenzene	0.18
1,2-dichloroethane	0.10	chloromethylbenzene	0.14
1,1,1-trichloroethane	0.05	*p*-dichlorobenzene	0.15
benzene	**0.06**	*o*-dichlorobenzene	0.17
carbon tetrachloride	0.06	1,2,4-trichlorobenzene	0.11
tert-amyl methyl ether	0.18	hexachloro-1,3-butadiene	0.15

[1]Experimentally determined (2002) according to 40 CFR Part 136 Appendix B.
Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

At least seven (usually 7 - 10) VOC standard canisters are prepared at the same concentration. A concentration that is one to five times the expected detection limit should be chosen. Using standards at a lower concentration will not necessarily provide lower MDLs. The VOC compounds analyzed by EPA Compendium Method TO-15 generally have detection limits at or below 0.20 ppbv. Therefore, the MDL study standard should be prepared at a concentration of 0.50 ppbv or lower. Each standard should be analyzed once with an injected volume equivalent to the sample volume analyzed; the standard deviation of each compound should be calculated for all of the analyses and should be multiplied by the applicable Student's t value, 3.143 for seven analyses, 2.998 for eight analyses, etc., to determine the MDLs consistent with 40 CFR Part 36 Appendix B. See Table 4.1-5 for applicable Student's t values.

Any analyzed concentrations below the MDL values should be flagged when the data are reported.

Table 4.1-5. Student's t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	Student's t Value
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

4.1.9.2 Replicate Precision

Analytical precision is estimated by repeated analysis of samples. Replicate analysis is performed on all duplicate or collocated samples taken in the field, (i.e., 10% of the total sample number). The RPD between the replicate analyses must be within 30%, except with compound concentrations less than five times the method detection limit for each compound. A replicate analysis that does not meet the criteria should be reanalyzed. The equation for percent difference is:

$$\text{relative percent difference} = \frac{(|X_1 - X_2|)}{X_{avg}} \times 100 \qquad (4.1\text{-}11)$$

Where:

X_1 = first measurement

X_2 = second measurement

X_{avg} = average of two measurements.

4.1.9.3 PE Accuracy

EPA will provide PE samples to program participants on a quarterly basis to verify the performance of the NATTS analytical systems. The equation for PE sample accuracy is:

$$\text{PE sample accuracy, \%} = \frac{|(\text{spiked value} - \text{observed value})|}{(\text{spiked value})} \times 100 \qquad (4.1\text{-}12)$$

4.1.10 Quality Control Specifications

QC specifications for the NATTS VOC program are presented in Table 4.1-6.

Table 4.1-6. Summary of Air Toxics TO-15 Quality Control Procedures

QC Check	Frequency	Acceptance Criteria	Corrective Action
BFB Instrument Tune Performance Check	Daily[1] prior to sample analysis	Evaluation criteria in Table 4.1-2 of this document.	1) Retune 2) Clean ion source and/or quadrupoles
Multipoint (at least five) calibration bracketing the expected sample concentrations.	Following any major change, repair or maintenance if daily QC is not acceptable. Recalibration period not to exceed three months.	1) RSD of response factors #30% 2) RRT for target peaks ±0.06 RRT units from mean RRT	1) Repeat an individual standard analysis 2) Repeat calibration curve 3) Prepare new calibration standards and repeat analysis
Calibration check using midpoint of calibration curve or one other point in curve.	Daily[1] on the days of sample analysis	Analyst verifies that the response factor #30% bias from calibration curve average response factor	1) Repeat calibration check 2) Repeat calibration curve
LCS (Second Source Standard)	Daily[1] on the days of sample analysis	Analyst verifies that the recoveries are 70% - 130%	1) Repeat analysis 2) Repeat calibration
System Blank Analysis	Daily[1] following BFB and calibration check; prior to analysis	1) <0.2 ppbv per analyte or the MDL, whichever is greater 2) IS area response ±40% and IS retention time ±0.33 min of most recent calibration check	1) Repeat analysis with new blank canister 2) Check system for leaks, contamination 3) Reanalyze blank
Duplicate and Replicate Analysis	All duplicate field samples	<30% RPD for compounds greater than 5 times MDL	Repeat sample analysis
Samples	All samples	IS area response ±40% of calibration mean and IS retention time ±0.33 min of calibration	Repeat analysis

[1]Every 24 hours frequency

4.2 OVERVIEW OF COMPENDIUM METHOD TO-11A

EPA Compendium Method TO-11A[6] will be applied to the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. EPA Compendium Method TO-11A[6] utilizes a coated solid adsorbent for collection of carbonyl compounds from ambient air followed by HPLC analysis with UV detection.

Carbonyl compounds, especially low molecular weight aldehydes and ketones, have received increased attention in the regulatory community due in part to their effects on humans and animals. Exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, and crotonaldehyde), even short term, has been proven to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. High concentrations of carbonyls, especially formaldehyde, can injure the lungs and may contribute to eye irritation and affect other organs of the body. Aldehydes may also cause injury to plants. Sources of carbonyl compounds in ambient air range from natural occurrences to secondary formation through atmospheric photochemical reactions.

In general, natural sources of carbonyls do not appear to be important contributors to air pollution. Aldehydes are commercially manufactured by various processes, including production of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds. Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years due in part to use of these compounds in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major industrial use of carbonyl compounds is as an intermediate in the syntheses of organic compounds, including alcohols, carboxylic acids, dyes, and medicinals.

A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde, the major carbonyl compound in automobile exhaust, accounts for 50 - 70% of the total carbonyl burden in the atmosphere. Furthermore, motor vehicles

also emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyl compounds in the atmosphere.

To address the need for a measurement method that determines carbonyl compounds with the sensitivity required to perform health risk assessments (i.e., 10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed. Activating or wetting the surface of an adsorbent with a chemical specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbent combinations have been utilized with various levels of success. The currently accepted technique, as applied to the NATTS Program, is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (DNPH) coated on a silica gel adsorbent cartridge, followed by separation and analysis of the hydrazone derivative by HPLC with UV detection. The methodology used to accomplish carbonyl compounds measurements is EPA Compendium Method TO-11A[6] (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf). EPA Compendium Method TO-11A provides sensitive and accurate measurements of carbonyl compounds and includes sample collection and analysis procedures. In this method, a cartridge(s) containing a coated solid sorbent is used to capture the compounds of interest. The sampling cartridge is extracted and the extract is analyzed using HPLC with UV detection.

Organic compounds that have the same HPLC retention time and significant absorbance at 360 nanometers (nm) (the absorption of the DNPH derivative of formaldehyde) will interfere. Such interferences can often be overcome by altering the chromatographic separation conditions (e.g., using alternative HPLC columns or mobile phase compositions).

Formaldehyde may be a contaminant in DNPH reagent. The use of commercially available precoated cartridges is required for the NATTS Program. For a commercial cartridge to be acceptable, formaldehyde background concentration should be less than 0.15 microgram (: g)/cartridge. For the enhanced carbonyl analysis, the following certification blank criteria must also be met for each lot of sampling cartridges:

- Acetaldehyde must be less than 0.10 : g/cartridge;
- Acetone must be less than 0.30 : g/cartridge; and
- All other carbonyl compound totals must be less than 0.10 : g/cartridge.

A "certification blank for formaldehyde" must be obtained for each lot of cartridges purchased.

The purity of the acetonitrile (ACN) used for the extraction of the sampling cartridges is an important consideration in the determination of allowable formaldehyde blank concentration in the reagent. Background concentrations of formaldehyde in ACN will be quantitatively converted to the hydrazone, adding a positive bias to the ambient air formaldehyde determinations.

Ozone has been identified as an interferent in the measurement of carbonyl compounds when EPA Compendium Method TO-11A[6] is used. To eliminate this interference, removal or scrubbing of O_3 from the sample airstream in the field is mandatory. Ozone at high concentrations has been shown to interfere negatively in the sampling process by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from O_3 has been observed at concentrations of formaldehyde and ozone typical of clean ambient air. Because of these issues, it is recommended that the ozone interference should be removed before the ambient air sample stream reaches the coated cartridge. This removal process entails constructing or purchasing an ozone denuder scrubber and placing it in front of the cartridge. The denuder scrubber is constructed using a saturated solution of potassium iodide (KI).

4.2.1 Sampling Procedure and Issues Associated with EPA Compendium Method TO-11A

Information and specifications applicable to conducting EPA Compendium Method TO-11A[6] for NATTS Program carbonyl measurements are presented below.

4.2.1.1 O_3 Scrubbers

The EPA has determined through laboratory tests that O_3 present in ambient air interferes with the measurement of carbonyl compounds when using EPA Compendium Method TO-11A[6]. O_3 can interfere with carbonyl analyses in three ways:

- The O_3 reacts with the DNPH on the cartridge and makes the DNPH unavailable for derivatizing carbonyl compounds;
- The O_3 also degrades the carbonyl derivatives formed on the cartridge during sampling and returns the carbonyl compounds to the more volatile underivatized state and contributes to a low bias in the analytical results; and
- If the analytical separation is insufficient, the DNPH degradation products can coelute with target carbonyl derivatives.

The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Carbonyl compound losses have been estimated to be as great as 48% on days when the ambient O_3 concentration reaches 120 ppbv. Eliminating this measurement interference problem by removing or scrubbing O_3 from the sample ambient air stream prior to collection of the carbonyl compounds is a mandatory facet of carbonyl compounds sample collection. Two types of O_3 scrubbers, the denuder O_3 scrubber and the cartridge O_3 scrubber, have been developed.[5] Both the denuder and cartridge O_3 scrubbers use KI as the scrubbing agent. Scrubbing is based on the reaction of O_3 with KI, specifically:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^- \quad (4.2\text{-}1)$$

Where:

O_3 = ozone (ambient)

H_2O = water (ambient)

I^- = the iodide ion from KI forming molecular iodine (I_2), oxygen (O_2), and the hydroxide ion (OH^-)

The denuder O_3 scrubber can effectively remove O_3 at sample collection flow rates up to 1 Lpm and has sufficient scrubbing capacity to meet the needs of carbonyl compounds measurement for enhanced O_3 monitoring programs; the cartridge O_3 scrubber is susceptible to plugging problems in the presence of moisture and is not applicable to the NATTS Program. Consequently, EPA has determined that, for the NATTS Program, only the denuder scrubber will be used. Details of the denuder O_3 scrubber equipment and recommended procedures for use are presented below.

4.2.1.2 Denuder O_3 Scrubber

The denuder O_3 scrubber consists of a copper tube coated internally with a saturated solution of KI. The tube is coiled and housed in a temperature-controlled chamber that is heated to and maintained at 50 - 70°C during sample collection. Heating prevents condensation from occurring in the tube during sampling. The scrubber is connected to the inlet of the sample collection system. Sample air is extracted from a sample probe and distribution manifold (see below) and pulled through the scrubber by an oil-free vacuum pump. O_3 in the sample air is converted (i.e., scrubbed) by the chemical reaction described above.

The denuder O_3 scrubber is reusable. The copper tube should be recoated with a saturated solution of KI after each six months of use. The denuder O_3 scrubber prepared as described in EPA Compendium Method TO-11A[6] has been found to effectively remove ozone from the air stream for up to 100,000 ppb-hours. Thus, the scrubber will last for six months of 24-hour

sampling on every sixth day when sampling air with an average O_3 concentration of 120 ppbv. If sampling frequency is increased, the usable period for the O_3 scrubber is proportionately decreased.

To recoat the denuder, the copper tube is filled with a saturated solution of KI in water. The solution should remain in contact with the tube for a few minutes, and then the tube should be drained. The tube should be dried by blowing a stream of clean air or nitrogen through it for about one hour.

An alternative to using a KI-coated copper tube is to use a modified Dasibi ozone scrubber device. The manganese-dioxide-coated screens are replaced with 15 KI-coated copper or stainless steel screens assembled in a cartridge holder. The screens are washed in pure water in a sonic bath and dried. The screens are then coated by dipping them into a saturated KI solution in water and air dried. This procedure deposits about 4 mmoles or about 700 milligrams (mg) of KI over a sandwich of 15, 2-in. diameter screens. The coated screens are assembled in the Dasibi encasement with a fiberglass filter at each end, and the encasement is closed and sealed including the O-rings with the screws. Based on this removal capacity, this scrubber will last approximately 300 days when sampling air with an average O_3 concentration of 120 ppbv at a rate of 1 Lpm.

Another alternative to using a KI-coated copper tube is the use of a commercially available KI-coated glass-coated denuder housed in a heated compartment. Manufacturers' specifications for longevity of the denuder should be followed carefully to ensure timely recoating or replacement.

Denuder O_3 Scrubber Equipment

Figure 4.2-1 presents a cross-sectional view of the denuder O_3 scrubber. The scrubber is comprised of the following components:

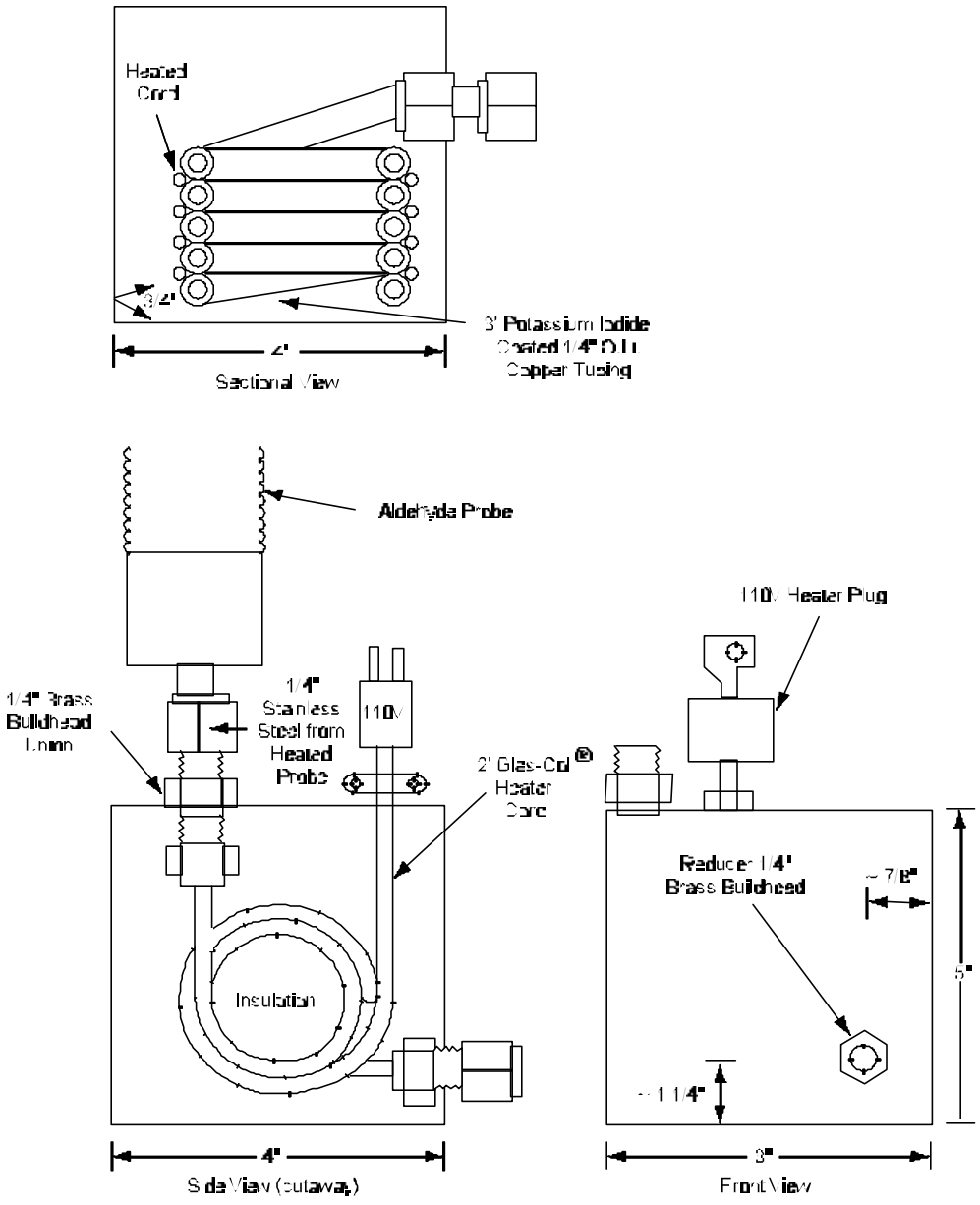

Figure 4.2-1. Cross-Sectional View of the Denuder O_3 Scrubber

- Copper tubing. One-fourth-inch o.d. copper tubing at least 36 in. length, coiled into a spiral approximately 2 - 4 in. diameter; used as the body of the O_3 scrubber.

- KI. The inside surface of the copper coil is coated with a saturated solution of ACS Reagent-Grade KI and is used to provide the O_3 scrubbing mechanism.

- Cord heater. A 2-foot long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil is used to provide heat to prevent condensation of water or organic compounds from occurring within the coil.

- Thermocouple. This Chromel-Alumel (Type K) thermocouple is located between the surface of the copper coil and the cord heater and is used to provide accurate temperature measurement for temperature control.

- Temperature controller. This Type K active temperature controller is used to maintain the O_3 scrubber at 66°C as referenced by the Type K thermocouple.

- Fittings. These are bulkhead unions attached to the entrance and exit of the copper coil; used to allow connection to other components of the sampling system.

- Chassis box. This box is a conveniently sized aluminum enclosure used to contain the fittings, coated copper tube, heater, and thermocouple.

4.2.1.3 Cartridge O_3 Scrubber

Although allowable under EPA Compendium Method TO-11A[6], use of cartridge O_3 scrubbers is not allowed for NATTS.

4.2.2 Sample Collection Systems

Sample collection systems should be capable of unattended operation in order to allow for single and duplicate sample collection in a practical manner. Sampling systems are manufactured commercially or can be custom manufactured by the user for a specific application; several sampling systems are commercially available. The following sections generally describe sampling equipment, procedures, and specifications. Also, recommended system specifications applicable to the evaluation and procurement of sampling systems are presented.

4.2.2.1 Sample Collection System Equipment

The cartridge sampling system consists of the following primary components:

- Inlet probe and manifold assembly. This assembly is constructed of glass or stainless steel and is used as a conduit to extract sample air from the atmosphere at the required sampling height and distribute it for collection.

- Bypass pump. This is a single- or double-headed diaphragm pump, or a caged rotary blower, used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

- Sample pump. This is an oil-free vacuum pump capable of achieving an inlet pressure of -25 in. Hg continually that is used to extract sample air from the manifold assembly and pull it through the sample cartridges during collection.

- Sample inlet line. This line is chromatographic-grade stainless steel or Teflon tubing used to connect the sampler to the manifold assembly that should be kept as short as possible.

- O_3 scrubber. This is a temperature-controlled denuder scrubber used to remove ambient O_3 from the sample airstream prior to exposure to the sample cartridge.

- Sample cartridge. This cartridge is a plastic housing containing silica gel solid sorbent (see Section 4.4 of EPA Compendium Method TO-11A) coated with DNPH that is used to contain the collected sample for transportation and analysis.

- Adjustable orifice and mass flow meter assembly, or electronic mass flow controller. This assembly is an indicating flow control device(s) used to maintain a relatively constant flow rate (±30%) over a specific sampling period under conditions of changing temperature (20 - 40°C) and humidity (0 - 100% relative).

- Digital timer or microprocessor. This is an event control device used to allow unattended operation (i.e., activation and deactivation of each sampling event) of the collection system.

- Tubing and fittings (stainless steel or Teflon). These are hardware for isolation and interconnection of components used to complete system interconnections. All stainless steel tubing in contact with the sample prior to analysis should be chromatographic-grade stainless steel, and all fittings should be 316-grade stainless steel. Note that if the manifold is heated, stainless steel tubing should be used because of the potential of off-gassing of tubing or other materials.

4.2.2.2 Carbonyl Sampling System Certification

Carbonyl sampling systems must exhibit nonbiasing characteristics before being used to collect samples. These sampling systems must be subjected to a laboratory zero certification to quantify any additive biases that may be attributed directly to the sampling systems. The certification procedure is analogous to the zero portion of the procedures used to certify canister sampling systems (Section 4.1.6). Specifically, the sampling system is characterized using humidified zero air. A humidified zero air blank to gauge the potential for additive bias is collected through the sampling system using the same conditions that will be applied to collect field samples. The blank sample is analyzed for specific NATTS Program carbonyl target analytes. The criteria applied to the zero certification process requires that the concentration determined for each target analyte species be 0.2 ppbv or less (a value consistent with a 1000-L sampling volume).

4.2.2.3 Sample Collection Procedures

Samples are collected on individual solid sorbent sample cartridges using a single pump and flow control device. An oil-free vacuum pump draws ambient air from the sampling probe and manifold assembly through the sample cartridge at a relatively constant flow rate during each specific sampling event.

A flow control device(s) is used to maintain a relatively constant sample flow rate through each sample cartridge over each specific sampling period. A nominal flow rate of 600 - 900 mL/min is applied for sample collection.

During operation, the control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of the sample collection period. Cartridge sampling systems can collect sample from a shared sample probe and manifold assembly or from a dedicated stainless steel sample probe, manifold assembly, and bypass pump. If a dedicated probe, manifold assembly, and bypass pump are used, a separate timer device

should be incorporated to start the bypass pump several hours prior to the first sampling event of a collection period to flush and condition the probe and manifold assembly components. The connecting lines between the manifold assembly and the sampling system should be kept as short as possible to minimize the system residence time.

The following generic steps are provided for operation of a typical collection system while collecting a sample:

1. Set the sampling system to the desired sample collection flow rate(s) (i.e., referencing the corresponding ambient calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event).

2. Program the digital timer control system to start and stop sample collection consistent with program specific collection frequency requirements.

3. Using vinyl gloves, attach the sample cartridge to the sampling system: one cartridge to collect a single sample, two cartridges for duplicate samples.

4. Record the start and end time of the collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate.

5. Using vinyl gloves, remove each sample cartridge (i.e., one at a time), cap both ends, and attach an identifier to each (i.e., again, one at a time to avoid mislabeling). Sample event number, sample type, location, and collection date should be recorded on the field data sheet.

6. Place cartridges in tightly enclosed transport containers and transport the samples and corresponding information to the central laboratory for preparation and analysis.

Calculation of method precision for the NATTS Program is determined by repeated analysis of duplicate samples. Consequently, 10% of all sample collections will be duplicate samples. A duplicate sample is a sample that is collected simultaneously with a primary sample (i.e., on two separate cartridges through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the inlet line of the sampler to each of the two cartridges. Each cartridge has its own associated flow control device to achieve integration over the 24-hour

collection period. A common pump pulls the sample through both collection cartridges (i.e., separately but simultaneously).

4.2.2.4 Collection System Specifications

Primary system specifications are presented below[5]. However, additional system specifications and considerations may be added at the discretion of the user.

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.

- The overall size of the sampling system should be kept as compact as possible. The sampling systems are usually installed into existing sampling site shelters where many other parameters (i.e., criteria pollutants concentrations, meteorological conditions, etc.) are also measured. Each of the other parameters requires separate instrumentation and consequently the shelters can become very crowded.

- The sample collection system should meet all applicable electrical and safety codes, operate on standard 110 volts of AC power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.

- The overall configuration and components comprising that configuration should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. The components themselves should generally conform to the descriptions presented above. All surfaces that come in direct contact with sampled air should be constructed of glass, stainless steel, Teflon, or Viton®.

- The sampling system must incorporate or provide for removal of O_3 consistently with the denuder O_3 scrubber design detailed above.

- The sampling system should incorporate a digital timer or microprocessor event control device. At a minimum this event control device should be able to be programmed to control the start and stop times of every collection event within a given 24-hour sampling duration. The event control device should incorporate a battery backup system to address power failure situations. Incorporation of a battery backup system should result in fewer invalidated sample collections and a higher sample collection completion rate. The battery backup system would ensure that all programmed control activities and collection process data would be retained for a predetermined interval should standard power to the system

be interrupted. Retaining the programmed control activities would allow sampling to resume automatically at the next programmed event time when standard power is once again established to the sampling system. Retaining the collection process data obtained for samples collected prior to the termination of standard power would allow these samples to be qualified as valid or invalid based on sampling start and stop times and initial and flow rates. Although not absolutely necessary, the incorporation of a miniature printer that would allow for a report style listing of all sample collection process data would be advantageous.

4.2.3 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field samples. Carbonyl compounds measured using EPA Compendium Method TO-11A[6] for the NATTS Program are shown in Table 4.2-1.

4.2.3.1 Analytical Interferences and Contamination

Contamination and interference can occur throughout the process from sampling to analysis and must be examined closely. Pure solvents and clean laboratories can prevent interference and contamination.

Solvents used in extractions and analysis must be high purity or reagent grade. ACN must be high purity and carbonyl free. If it is not, higher concentrations of formaldehyde during

Table 4.2-1. Carbonyl Compounds Measured Using EPA Compendium Method TO-11A[6]

Compound	CAS No.
formaldehyde	**50-00-0**
acetaldehyde	75-07-0
acetone	67-64-1
propionaldehyde	123-38-6
crotonaldehyde[1]	4170-30-3
butyr/isobutyraldehyde	123-72-8
benzaldehyde	100-52-7
isovaleraldehyde	590-86-3
valeraldehyde	110-62-3
o-tolualdehyde	529-20-4
m-tolualdehyde	620-23-5
p-tolualdehyde	104-87-0
hexaldehyde	66-25-1
2,5-dimethylbenzaldehyde	5779-94-2

[1]Analytical problems similar to those of acrolein are encountered with crotonaldehyde.
Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

analysis of samples and blanks can result. All glassware must be washed, rinsed with deionized distilled water, allowed to dry, then rinsed again with ACN and baked in a vacuum oven at 60°C for 30 min. Burdick & Jackson®, carbonyl-free ACN meets all quality specifications of the methodology.

Acetone vapors found in the laboratory during extraction will also cause inaccurate concentrations of compounds during analysis. Acetone is found in many common items such as permanent markers, felt tip pens, paint, etc. It is therefore necessary to keep all acetone products out of the laboratory. Acetone is also encountered when laboratory facilities are shared; additional precautions will be required to mitigate acetone contamination during extraction.

4.2.3.2 Extraction and Chromatography Issues

Each carbonyl cartridge should be examined closely before extracting. Cartridges that are leaking silica gel must be voided. Cartridges that are dark orange or reddish contain moisture and should be firmly tapped several times before extraction. These samples must be flagged in the extraction log as they may need to be diluted. Once extraction has occurred, the extract should also be examined. Any solution with noticeable particles must be filtered before the sample can be analyzed to prevent clogging the HPLC filters, frits and tubing.

Due to the acidity of the cartridge, the compound acrolein becomes unstable and breaks down into other hydrocarbons; this breakdown makes quantitation based on a single peak inaccurate. Therefore, EPA Compendium Method TO-11A[6] may not be suitable for the detection of this compound.

The chromatogram of each sample must have a DNPH peak to indicate that unreacted reagent is still available on the cartridge (i.e., the capacity of the cartridge for the collection of carbonyl compounds has not been exceeded). This DNPH peak occurs at approximately 4.4 min into the HPLC chromatogram and is usually the highest peak on the chromatogram. If there is no DNPH peak, the reagent has been expended and the sample must be voided because collection of the carbonyl compounds may not have been quantitative. Exhaustion of the derivatization reagent is an indication of high concentrations of aldehydes/ketones at the site and an insufficient amount of DNPH within the cartridge for complete derivatization. If the DNPH peak is smaller than usual and the aldehyde/ketone peak concentrations are not above the highest level of the curve, the sample is valid.

4.2.3.3 Sample Preparation

Once sampling has occurred, the field samples and field blanks are shipped back to the laboratory in individual, sealed foil pouches. Upon receipt of the samples, each sample and field blank is given an ID number, placed in a sealable bag with a COC and stored in a refrigerator at

<4ºC until extraction. Extraction should occur within two weeks of the sampling episode. For remote sites involving great travel distances and long travel times, extraction must still occur within two weeks of sampling.

Sample Extraction

Field samples and a blank cartridge of the same lot are removed from the refrigerator and connected to a clean, solid phase extraction manifold. A glass syringe is attached to the cartridge, and 5 mL of ACN is back flushed from the syringe through the cartridge and into a 5-mL volumetric flask. A polypropylene syringe may be substituted for the glass syringe, but the polypropylene syringe MUST be considered disposable—i.e., discarded after a single use. The flask is then diluted with ACN to the 5-mL mark. This extract is transferred to vials for analysis and cold storage (4ºC). Samples must be analyzed within 30 days of extraction. An extraction log with the site code, sample date, identification number and comments section is kept for each sample. This log is permanently affixed in a logbook and kept in the laboratory.

4.2.3.4 Preparation of the Analytical System

Operating parameters for HPLC when formaldehyde is the compound of interest are described in Section 11.3.1 of EPA Compendium Method TO-11A.[6] Samples are analyzed on the HPLC, Waters 2695 separations module, or equivalent, with a Zorbax C18 reversed phase column and guard column. The 2487 dual wavelength absorbance detector is set at 360 nm and must be allowed to warm up for 30 min before analysis is performed. Deionized distilled water, ACN and methanol used in the analyses should be HPLC grade, and each must be sonicated or degassed with helium prior to use. The HPLC grade water is filtered through a 0.2-:m nylon membrane filter to eliminate microbial growth. Solvent should pump at the desired flow rate of 1 to 2 mL/min for 30 min. Prior to the first injection, system pressure should remain constant. A higher than normal pressure indicates a clogged in-line filter or guard column. Once the system has stabilized, calibration may begin. Other HPLC instruments, like the Hewlett-Packard LC-1050

with diode array detector, have also been used in aldehyde and ketone analysis under similar conditions.

Initial Calibration

HPLC calibration is performed using commercially prepared stock solutions ranging from 0.01 to 0.5 µg/mL of each target analyte purchased as a DNPH derivative of the carbonyl compound. These solutions are stable up to 6 months from the date opened. Each calibration standard (at least five levels) is analyzed three times, and area response is tabulated against mass concentration injected to prepare a calibration curve. The slope of the curve (instrument response per sample concentration) yields the response factor (RF). Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least squares fit of the data is obtained. A commercially prepared standard from a second vendor is also analyzed three times to evaluate precision and to validate each new curve. Repeated analysis of this second source standard is used as the mid-level standard to evaluate precision, peak resolution and retention time drift throughout the life of the calibration curve. For calculations, refer to Section 12 of EPA Compendium Method TO-11A.[6] The multipoint calibration is performed at least once every 6 months to verify the precision and calibration range. A new multipoint calibration curve is also required if the column is changed on the instrument, major maintenance is performed on the instrument or there is a change in the matrix or a reagent.

Acceptance Criteria for Initial Calibration Curve

The following criteria must be met for an acceptable initial calibration curve:

- Each analyte must have a correlation coefficient of greater than or equal to 0.999.
- The relative percent error for each triplicate level should be within 20% of the theoretical concentration

$$\text{Relative Percent Error} = \frac{\text{TLC - OLC}}{\text{TLC}} * 100 \qquad (4.2\text{-}2)$$

Where:

TLC = theoretical level of concentration

OLC = observed level of concentration

- The second source quality control (SSQC) sample must be within 15% of target concentrations.
- The intercept should be #10,000 area counts per compound, for the current setup of the Waters 2695 HPLC.

4.2.3.5 Process Blanks

To ensure data quality and obtain quantitative carbonyl compound concentrations, the collection of blanks is necessary. For national air toxics monitoring there are three types of blanks used to ensure data quality: certification blanks, field blanks and method blanks. The guidance here should be considered a minimum and users are encouraged to build upon this guidance.

- Certification blanks consist of three commercially prepared DNPH-coated, prepacked cartridges that are eluted with ACN and analyzed to verify the acceptability of a specific cartridge lot from the vendor. Certification blanks are analyzed for each specific lot used for sampling. Alternatively, a "Certificate of Analysis" accompanying each lot may be used for certification as long as it meets the blank acceptance criteria.
- Field blanks are blank cartridges which are sent to the field, connected to the sampling system and treated identically to the samples except that no air is drawn through the cartridge. Field blanks are used to assess the background carbonyl levels for cartridges used during the ambient sample collection process.
- Method blanks are blank cartridges that never leave the laboratory and are extracted with every batch of samples. Method blanks are used to assess possible laboratory contamination.

- If evaluation of the potential for contamination in the shipping process is desired, a trip blank may be used. A trip blank is shipped to and from the field but is not opened until it is extracted in the laboratory.

Acceptance Criteria for Blanks

A "Certificate of Analysis"accompanying each lot of DNPH-coated, prepacked cartridges may be used for certification as long as it meets the blank acceptance criteria. If the values in the "Certificate of Analysis" do not meet acceptance criteria, three laboratory blanks from that lot must be analyzed and meet blank acceptance criteria. If the mean mass ±3 standard deviations ($\bar{x} \pm 3$ s) for the group of three laboratory blanks meets the criteria, no further certification of laboratory blanks is required for that particular cartridge lot. If large differences are observed for the three laboratory blank samples, additional laboratory blanks should be analyzed to obtain values for the mean and standard deviation. If the certification blanks or the "Certificate of Analysis" do not meet the specified blank acceptance criteria, the carbonyl tubes should be shipped back to the manufacturer and a new lot requested. For certification blanks or the "Certificate of Analysis" to be acceptable, the following criteria must be met:

- Formaldehyde: < 0.15 : g/cartridge
- Acetaldehyde: < 0.10 : g/cartridge
- Acetone: < 0.30 : g/cartridge
- Other: < 0.10 : g/cartridge.

For field blanks to be acceptable, the following criteria must be met:

- Formaldehyde: < 0.3 : g/cartridge
- Acetaldehyde: < 0.4 : g/cartridge
- Acetone: < 0.75 : g/cartridge
- Sum of others: < 7.0 : g/cartridge.

If a field blank does not meet the criteria and the corresponding sample has concentrations above the average mean from the previous year, the sample is blank subtracted and flagged on the report. If the corresponding sample concentration is not high, the sampling site is notified so that another field blank can be scheduled. Field blank sampling should continue until the sample passes the criteria.

The following criteria must be met for method blanks:

- Formaldehyde: < 0.10 : g/cartridge
- Acetaldehyde: < 0.20 : g/cartridge
- Acetone: < 0.55 : g/cartridge
- Sum of others: < 3.00 : g/cartridge.

If the method blank fails to meet acceptance criteria, that method blank should be reanalyzed and the laboratory checked for signs of possible contamination. If the analysis still fails to meet acceptance criteria, the samples are blank subtracted and flagged on the report.

4.2.3.6 Precision and Accuracy

For 10% of field collections, samples must be collected in duplicate. A primary and a duplicate sample are collected from a common manifold and sample inlet line using the same sampling system but two independent flow control devices. Duplicate samples must be analyzed in replicate. Replicate analyses of the duplicate samples should agree to within 10% for concentrations < 0.5 : g/cartridge and the means of the replicate analyses for the duplicate samples should agree to within 20%. If the means of the duplicate samples do not agree to within 20% and the replicate analyses are within 10%, check the samples to ensure that they are truly duplicate, check the sample flow rates to ensure that the sampler is working correctly and check chromatography to make sure peaks are integrated correctly. If both sampler and chromatography

are acceptable, repeat the sample analysis. Precision is determined as the RPD using the following calculation:

$$RPD = \frac{*X1 - X2*}{\bar{x}} \times 100 \qquad (4.2\text{-}3)$$

Where:

X1 = ambient air concentration of a given compound measured in one sample

X2 = concentration of the same compound measured during replicate analysis

$\bar{x}$ = arithmetic mean of X1 and X2.

Accuracy will be assessed by quarterly analysis of a PE sample supplied by EPA.

4.2.3.7 Method Detection Limits

Minimum MDLs that must be achieved for the NATTS Program are presented in Table 4.2-2. MDLs are determined at least annually using the procedures in 40 CFR Part 136 Appendix B. A low-level standard of the carbonyl derivatives is prepared at a concentration within two to five times the estimated method detection limit. Commercially prepared DNPH-coated, prepacked cartridges (7 - 10) are spiked with the standard. Spiked tubes are extracted as explained in Section 4.2.3.3. The measured concentration is calculated using the calibration curve. The concentration of derivatized aldehyde/ketone in the sample is calculated below:

$$C = \frac{(SR - I)}{S} \qquad (4.2\text{-}4)$$

Where:

C = concentration of derivatized compound (: g/mL)

SR = sample response area units

I = intercept of calibration curve

S = slope of calibration curve.

The standard deviation is calculated for the number of samples analyzed; the standard deviation and the appropriate Student's t value are used to calculate the MDL as described in 40 CFR Part 136 Appendix B. Table 4.2-2 presents Student's t values for different degrees of freedom. MDLs should be calculated in units of ppbv reflecting different collection volumes across the range of 800 L through 1300 L, as shown in Table 4.2-3.

Table 4.2-2. Student's t Values Used in Calculation of Method Detection Limits

Number of Replicates	Degrees of Freedom (n - 1)	t Values
7	6	3.143
8	7	2.996
9	8	2.896
10	9	2.821

Table 4.2-3. MDLs for Carbonyl Data for the NATTS Program[1]

Compound (ppbv)	Sample Volume (L)					
	800	900	1000	1100	1200	1300
formaldehyde	0.035	0.031	0.028	0.0257	0.0235	0.0217
acetaldehyde	0.023	0.020	0.018	0.0164	0.0150	0.0138
acetone	0.012	0.011	0.010	0.0087	0.0080	0.0074
propionaldehyde	0.011	0.010	0.009	0.0083	0.0077	0.0071
crotonaldehyde	0.017	0.015	0.013	0.0121	0.0110	0.0102
butyr/isobutyraldehyde	0.084	0.075	0.067	0.0613	0.0562	0.0519
benzaldehyde	0.004	0.004	0.003	0.0032	0.0029	0.0027
isovaleraldehyde	0.003	0.003	0.003v	0.0025	0.0023	0.0021
valeraldehyde	0.004	0.003	0.003	0.0028	0.0026	0.0024
tolualdehydes	0.007	0.006	0.006	0.0052	0.0048	0.0044
hexaldehyde	0.006	0.005	0.005	0.0045	0.0041	0.0038
2,5-dimethylbenzaldehyde	0.003	0.003	0.002	0.0021	0.0019	0.0018

[1]Experimentally determined (2002) according to the procedures of 40 CFR Part 136 Appendix B.

4.2.3.8 Sample Analysis

When the calibration and MDLs meet acceptance criteria, the instrument is ready to analyze samples. The autosampler vials are placed in a carousel and loaded onto the instrument. An injection size of sample extract geared to the manufacturer's specifications for the analytical instrument is performed with an automatic sample injector. A mobile phase gradient of water, ACN and methanol is used to perform the analytical separation at a flow rate of 1.0 mL/min. Each sequence loaded onto the instrument must start with an ACN instrument blank followed by a QC standard, another ACN instrument blank, the method blanks for each lot of samples to be analyzed followed by the samples. A QC standard must be analyzed every 12 hours to ensure that the instrument is within calibration and the retention times for the compounds have not shifted. The sequence is completed with a third ACN instrument blank, a final QC standard and a final ACN instrument blank. For the ACN to meet acceptance criteria, the compound concentrations must be less than or equal to 5 times the method detection limits. Carbonyl QC procedures are presented in Table 4.2-4.

4.2.3.9 Method Spikes

A method spike and method spike duplicate, consisting of coated sorbent spiked with derivatized aldehydes/ketones, must be analyzed once every quarter to verify calibration and extraction procedures. A 1-mL aliquot of the QC Standard is transferred to a 5-mL volumetric flask, diluted to volume with ACN and mixed. This solution is used to spike cartridges (1 mL per cartridge) for these tests. The spike and spike duplicate should be within ±20% of the target concentration. If the concentrations are outside these limits, the calibration and extraction procedures are checked. If the calibration and extraction procedures are acceptable, the analysis is repeated. Carbonyl QC procedures are presented in Table 4.2-4. An SSQC sample is a sample of known concentration prepared by an organization different from the analyzing laboratory or the supplier of the calibration standards. The SSQC must contain all of the analytes of interest at a known concentration.

Table 4.2-4. Summary of Carbonyl Quality Control Procedures[2]

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
HPLC Column Efficiency	Analyze SSQC sample	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde $ 1.0 Column efficiency > 5000 plate counts	Eliminate dead volume, back flush or replace the column; repeat analysis
Linearity Check	Run a 5-point calibration curve and SSQC in triplicate per Method TO-11A	At setup or when calibration check is out of acceptance criteria	Correlation coefficient $ 0.999, relative error for each level against calibration curve ±20% or less relative error	Check integration, reintegrate or recalibrate
			Intercept acceptance should be #10,000 area counts per compound which correlates to ~0.06 mg/mL	Check integration, reintegrate or recalibrate
Retention Time	Analyze SSQC	Once per 12 hours or less	Acetaldehyde, benzaldehyde, hexaldehyde within retention time window established by determining 3F or ±2% of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature; check gradient and solvents
Calibration Check	Analyze SSQC	Once per 12 hours or less	85 - 115% recovery	Check integration, recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard
Calibration Accuracy	Analyze SSQC	Once after calibration in triplicate	85 - 115% recovery	Check integration, recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard
System Blank	Analyze ACN	Bracket sample batch, 1 at beginning and 1 at end of batch	Measured concentration # 5 times the MDL	Locate contamination and document levels of contamination in file

(Continued)

Table 4.2-4. (Continued)

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
Lot Blank Check	Analyze blank cartridge for new lots	Every lot received	Compounds must be less than values listed: Formaldehyde <0.15 : g/cartridge Acetaldehyde <0.10 : g/cartridge Acetone <0.30 : g/cartridge Others <0.10 : g/cartridge	Analyze another cartridge. Notify vendor if lot blank continues to fail. Failed lots are not used for sampling.
Field Blank Check	Field blank samples collected in the field	#10% of the sampling schedule	Compounds must be less than values listed: Formaldehyde <0.4 : g/mL derivatized <0.3 : g/cartridge underivatized Acetaldehyde <0.4 : g/mL derivatized <0.4 : g/cartridge underivatized Acetone <0.6 : g/mL derivatized <0.75 : g/cartridge underivatized Others <0.10 : g/mL derivatized <7.0 : g/cartridge underivatized	Data associated with an unacceptable Field Blank are flagged. Additional Field Blanks are collected until the problem is resolved.
Duplicate Analyses	Duplicate and replicate samples	10% of the sampling schedule	<20% difference as RPD	Check integration, check instrument function, reanalyze duplicate samples
Replicate Analyses	Replicate injections	Duplicate samples only	# 10% RPD for concentrations greater than 0.5 : g/cartridge.	Check integration, check instrument function, reanalyze duplicate samples
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD, using calibration standard	One MS/MSD per quarter year	80 - 120% recovery for all compounds	Check calibration, check extraction procedures
PE Samples		Quarterly	No specific acceptance criteria; evaluation of performance is goal	To be determined by EPA

4.2.3.10 Data Reduction, Validation and Reporting

A sample analysis logbook is maintained to list pertinent sample information at the time of analysis. Entries include site code, sample date, analysis date and electronic file names. A data system, such as PE Turbochrome, HP Chemstation or equivalent, is needed to acquire, integrate, quantitate and store the analytical data. Preliminary peak identifications are determined based on elution times. A data reviewer compares the sample chromatogram and the QC chromatogram to determine proper peak identifications and determine whether reintegration is needed on any peak. If the concentration of an analyte exceeds the linear range of the instrument, the sample is diluted with ACN and reanalyzed. Only the diluted value is reported for that compound and flagged on the data report. Quantitation is based on raw amounts of analyte in µg/mL calculated by the data system from the curve. Results in ppbv are then calculated as described below.

$$ppbv = \frac{\text{raw amount (µg/mL)} * 122{,}000}{V * MW} \qquad (4.2\text{-}5)$$

Where:

122,000 = (24.4 µL/µMole * 5 mL (volume) * 1000 (conversion factor from microliters to nanoliters)

MW = molecular weight of analyte (µg/µMole)

V = volume of air collected in liters (ambient conditions).

Once the chromatograms have been reviewed, the data are transferred to a summary database such as Excel® for review. The analytical data reviewer examines all data for overall quality and completeness. When the final review is complete, a chromatogram and area count report are printed out and stored in a folder with the COC form. Sample files are stored by sample date in a specified data storage room. Electronic copies of the data are stored on a removable disk hard drive and saved on compact disk for an electronic data archive.

4.3 OVERVIEW OF EPA COMPENDIUM METHOD IO-3.5

EPA Compendium Method IO-3.5[7] (http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf) is the measurement method used for sampling and analytical procedures for the measurement of metals in ambient air. The method involves collection on filters and detection by inductively coupled plasma/mass spectrometry (ICP/MS). ICP/MS uses an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows many more than 60 elements to be quantitatively determined simultaneously, and the isotopes of an element can also be determined.

4.3.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities (ICP/MS)

EPA Compendium Method IO-3.5[7] describes the multielement determination of trace elements by ICP/MS. Ambient air is pulled through filter media using a high volume sampler. Particulate phase sample is collected on the filter, and the filter is digested yielding the sample material in solution. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier, and the ion information is processed by a data handling system.

4.3.2 Sampling Procedures and Issues Associated with EPA Compendium Method IO-3.5[7]

Sample collection for quantitative determination of metal species is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter over a

24-hour collection period.

4.3.2.1 Sample Collection Procedure

The sample collection is performed using a commercially available TSP high volume sampling system capable of maintaining a flow rate of approximately 1.1 to 1.7 scmm (39 - 60 ft^3/min) through a filter to obtain a total sample volume greater than 1584 scm across a 24-hour duration. TSP in sizes up to 25 - 50 :m (aerodynamic diameter) is collected on the filter surface.

The glass fiber filter is 8 in. x 10 in. and is constructed of spectro-quality grade glass fiber material with a pH of approximately 7.5. The filters must have a collection efficiency of $99% for particles of 0.3 :m in diameter or larger. Each filter must have a unique ID number that is a permanent part of the filter.

The sampler should be located in an unobstructed area at least 2 m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 - 10 feet above ground level.

Similar to monitoring for other pollutants, optimal placement of the sampler inlet for PM_{10} monitoring should be at breathing height level. However, practical factors such as prevention of vandalism, security, and safety precautions must also be considered when siting a PM_{10} monitor. Given these considerations, the sampler inlet for microscale PM_{10} monitors must be 2 - 7 m above ground level. The lower limit was based on a compromise between ease of servicing the sampler and the desire to have measurements which are most representative of population exposures and the desire to avoid reentrainment from dusty surfaces. The upper limit represents a compromise between the desire to have measurements which are most representative of population exposures and a consideration of the practical factors noted above. Although microscale or middle scale stations are not the preferred spatial scale for $PM_{2.5}$ sites, there are situations in which such sites are representative of several locations within an area where large segments of the population may live or work (e.g., central business district of a metropolitan area). In these cases, the sampler inlet for such microscale $PM_{2.5}$ stations must also be 2 - 7 m above

ground level. For middle or larger spatial scales, increased diffusion results in vertical concentration gradients that are not as great as for the microscale. Thus, the required height of the air intake for middle or larger scales is 2 - 15 m.

If the sampler is located on a roof or other structure, there must be a minimum of 2 m of separation from walls, parapets, penthouses, etc. No furnace or incineration flues should be nearby. This separation distance from flues is dependent on the height of the flues, type of waste or fuel burned, and quality of fuel (ash content). In the case of emissions from a chimney resulting from natural gas combustion, as a precautionary measure, the sampler should be placed at least 5 m from the chimney. On the other hand, if fuel oil, coal, or solid waste is burned and the stack is sufficiently short so that the plume could reasonably be expected to impact on the sampler intake a significant part of the time, other buildings/locations in the area that are free from these types of sources should be considered for sampling. Trees provide surfaces for particulate deposition and also restrict airflow. Therefore, the sampler should be placed at least 20 m from the drip line and must be 10 m from the drip line when the tree(s) acts as an obstruction. The sampler must also be located away from obstacles such as buildings, so that the distance between obstacles and the sampler is at least twice the height that the obstacle protrudes above the sampler except for street canyon sites. Sampling stations that are located closer to obstacles than this criterion allows should not be classified as neighborhood, urban, or regional scale, since the measurements from such a station would closely represent middle scale stations. Additional information for siting samplers is provided in 40 CFR Part 58 Appendix E.[8]

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Reference Method, *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)* (EPA-600/4-77-027a)[9]. The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented using a U-tube manometer. The differential pressure readings are used to create a curve that establishes the flow characteristics of the sampler.

The following generic steps are provided for operation of a typical high volume collection system:

1. Install a preweighed filter in the sampler according to the detailed instructions in Section 4.0 of the reference method[9], taking care to align the filter correctly. The individual identification number of the filter must not face into the gas flow so that particulate material will not obscure the sample identifier.

2. Close the shelter and run the sampler for at least 5 min to establish run temperature conditions.

3. Record the initial flow indicator reading, the barometric pressure, and the ambient temperature; then stop the sampler.

4. Determine the flow rate from the sampler's calibration relationship to verify that it is operating in the acceptable range. Record the sample identification information and the initial flow rate on the field data form.

5. Set the timer to run the sampler for 24 hours, from 12:00 a.m. to 11:59 p.m.

6. After the sample has been collected, close the shelter and run the sampler for at least 5 min to establish final run temperature conditions.

7. Record the final flow indicator reading, the barometric pressure, and the ambient temperature; then turn the sampler off.

8. Determine the flow rate from the sampler's calibration relationship to calculate the total volume of gas sampled.

9. Remove the filter and fold the filter in two onto itself (particulate-sampled sides facing) so that none of the particulate mass is lost.

10. Place the folded filter in an appropriately sized envelope for transport to the laboratory.

4.3.3 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all of the procedures involved in the analysis of field samples. Metals measured using EPA Compendium Method IO-3.5 for the NATTS Program are presented in Table 4.3-1.

Table 4.3-1. Metals Measured Using EPA Compendium Method IO-3.5

Metals	CAS No.
antimony and compounds	7440-36-0
arsenic and compounds	**7440-38-2**
beryllium and compounds	7440-41-7
cadmium and compounds	7440-43-9
chromium and compounds	7440-47-3
cobalt and compounds	7440-48-4
lead and compounds	7439-92-1
manganese and compounds	7439-96-5
mercury and compounds	7439-97-6
nickel and compounds	7440-02-0
selenium and compounds	7780-49-2

Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

4.3.3.1 Interferences and Contamination

Interferences relating to this technique must be recognized and corrected. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, air, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected by internal standardization.

Isobaric elemental interferences are caused by isotopes of different elements that form single- or double-charged ions of the same nominal mass-to-charge ratio and therefore cannot be resolved by the mass spectrometer. Any record of this correction process should be included with the report of the data. These corrections will be only as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

Abundance sensitivity is the property defining the degree to which the wings of a mass peak contribute to adjacent masses. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that has the same nominal mass-to-charge ratio as the isotope of interest and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gasses or sample components. Equations for the correction of data should be established at the time of analytical run sequence because the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass-spectrometer interface. Internal standardization may be effectively used to compensate for many physical interference effects. ISs ideally should have analytical behavior similar to that of the elements being determined.

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. These interferences can result from sample deposition on the sampler and skimmer cones and from the buildup of sample material in the plasma torch and spray chamber. The possibility of memory interferences should be recognized within an analytical run, and suitable rinse times between samples should be used to reduce them.

4.3.3.2 Sample Preparation

This section describes both a microwave digestion procedure and a hot acid digestion procedure to extract inorganic elements from the particulate quartz glass fiber filter. Following digestion, target analytes are analyzed by ICP/MS.

Sample Receipt

Ambient air quartz fiber filters should be received folded in half lengthwise with the particulate material inward and with the entire filter enclosed in a protective envelope. These protective envelopes are stored at approximately 15 - 30°C until analysis. The maximum sample holding time is usually 180 days.

Filter Cutting Procedure

A strip 1 in. × 8 in. is cut from the filter using a template and cutting tool as described in the FRM for lead. A laboratory microwave is used to extract the metals with a hydrochloric/nitric acid solution. After cooling, the digestate is mixed and filtered through a syringe filter to remove any insoluble material.

Digestion Procedure: Microwave Digestion for Ambient Filters

Note: Nitric and hydrochloric acid fumes are toxic. Samples must be prepared in a well-ventilated fume hood. Mixing of the acids results in an exothermic reaction; acids should be stirred slowly.

The filter strip is retrieved and placed on its edge in a labeled centrifuge tube with vinyl gloves or plastic forceps. The filter is crushed with the plastic forceps into the lower portion of the centrifuge tube to ensure that the acid volume will cover the entire filter. The samples are digested in the microwave and cooled, and water is added to produce a final volume of 20 mL for analysis.

More than one strip from a filter should be digested to ensure adequate sample volume for sample and QC sample analysis. Blank filter samples should be digested and analyzed, and digestion blanks should be prepared to ensure low levels of metals in the reagents used.

Digestion Procedure: Hot Acid Digestion for Ambient Filters

The hot acid procedure is used as an alternate when microwave technology is not available. With vinyl gloves or plastic forceps, the filter strip is placed in a 150-mL Griffin beaker; the filter is placed in the lower portion of the beaker to ensure that the acid volume will cover the entire filter. Acid is added and the beaker is placed on a hot plate in a fume hood and refluxed for 30 minutes. Water is added to the cooled sample, and the fluid in the beaker is transferred to a 20-mL volumetric flask. Filter the digestate; the final volume is 20 mL of filtered digestate.

More than one strip from a filter should be digested to ensure adequate sample volume for sample and QC sample analysis. Blank filter samples should be digested and analyzed, and digestion blanks should be prepared to ensure low levels of metals in the reagents used.

4.3.3.3 Standard and QC Sample Preparation

Standard stock solutions may be purchased from a commercial source or prepared from ultra-high-purity grade chemicals or metals (99.99% or greater purity). The standards must include every metal of interest. Stock solutions should be stored in Teflon bottles.

When multielement standard solutions are prepared, care should be taken to ensure that the elements are compatible and stable. Originating element stocks should be checked for impurities that might influence the accuracy of the standard. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response. Concentrations of 200 : g/L are suggested.

Internal Standards

ISs are prepared by diluting 10-mL stock standards of scandium, yttrium, indium, terbium, and/or bismuth stock standards to 100 mL with deionized water and storing these standards in a Teflon bottle. This solution concentrate is used to spike blanks, calibration standards, and samples or is diluted by an appropriate amount using 1% (v/v) nitric acid. These internal standards are normally added using a peristaltic pump.

Blanks

Three types of blanks are required for this method. A calibration blank establishes the analytical calibration curve and consists of 1% (v/v) nitric acid in deionized water. The laboratory reagent blank (LRB) assesses possible contamination from the sample preparation procedure and spectral background. The LRB must contain all of the reagents in the same volumes as used in processing the samples and must be carried through the entire sample digestion and preparation scheme. The rinse blank flushes the instrument between samples to reduce memory effects and consists of 2% (v/v) nitric acid in deionized water.

Tuning Solution

A tuning solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions in 1% (v/v) nitric acid to produce a concentration of 100 : g/L of each element. ISs are not added to this solution.

QC Sample

A QC sample is obtained by diluting an appropriate aliquot of a second source standard in 1% (v/v) nitric acid.

Laboratory Fortified Blank

A laboratory fortified blank (LFB) is prepared by adding an aliquot from the multi-element stock standards to produce the LFB with a final concentration of 100 : g/L for each analyte. The LFB must be carried through the entire sample digestion and preparation scheme.

4.3.3.4 Calibration

Demonstration and documentation of acceptable initial calibration are required before samples are analyzed and then periodically throughout sample analysis as dictated by results of continuing calibration checks. After the initial calibration is successful, a calibration check is required at the beginning and end of each period during which the analyses are performed and at requisite intervals.

After the instrument has warmed up for at least 30 minutes, mass calibration and resolution checks using the tuning solution must be conducted. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For good performance, spectrometer resolution should be adjusted to produce a peak width of approximately 0.75 amu at a 5% peak height. Mass calibration should be adjusted if it has shifted by more than 0.1 amu from unit mass.

Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

The instrument must be calibrated for the analytes to be determined using the calibration blank and calibration standards prepared at multiple concentration levels. A minimum of three replicate integrations at each concentration level is required.

A rinse blank should be used to flush the system between solution changes for blanks, standards, and samples. Sufficient rinse time should be allowed to remove traces of the previous sample. To establish equilibrium, solutions should be aspirated for at least 30 seconds prior to the acquisition of data.

4.3.3.5 Internal Standards

Internal standardization must be used to correct operational anomalies, including instrument drift and physical interferences. Metals commonly used as ISs include scandium, yttrium, indium, terbium, and/or bismuth. For a full mass range scan, a minimum of three ISs must be used. ISs must be present in all samples, standards, and blanks at identical levels and may be included either by directly adding an aliquot of the IS to the calibration standards, blank and sample solution or by mixing the IS with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the IS should be sufficiently high to obtain a precise measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A concentration of 200 : g/L of each IS is recommended.

4.3.3.6 Instrument Procedure

After establishing calibration, a QC sample must be verified before analysis may be conducted. If replicate measurements of the QC sample exceed ±10% of the theoretical value, the analyst should identify and correct the problem, recalibrate if necessary and verify again with another QC sample.

Calibration blanks and standards should be run after every 10 samples to verify calibration on a continual basis. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, analysis of the standard is repeated. If the analyte is again outside the 10% limit, the instrument must be recalibrated and the previous ten samples reanalyzed. If the sample matrix is responsible for the calibration drift, the previous 10 samples

should be reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

4.3.4 QC

Each laboratory analyzing filters following EPA Compendium Method IO-3.5 is required to operate a formal QC program. The minimal requirement of such a program is an initial demonstration of laboratory capability and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data generated.

4.3.4.1 Precision

For 10% of field collection episodes, collocated samples must be obtained. A primary and a collocated sample are collected using two independent sampling systems. Collocated sample pairs must be analyzed in replicate. Replicate analyses of the collocated sample pairs should agree to within ±10%, and the means of the replicate analyses for the collocated sample pairs should agree to within ±20%. If the collocated sample pairs do not agree to within ±20% and the replicate analyses are within ±10%, the samples should be checked to ensure that they are truly collocated and collected over the same time period, the sample flow rates should be checked to ensure that the samplers are working correctly and the raw data should be checked to make sure values are integrated and calculated correctly. Precision is determined as the RPD using the following calculation:

$$RPD = \frac{*X1 - X2*}{\theta} \times 100 \qquad (4.3\text{-}1)$$

Where:

X1 = ambient air concentration of a given metal measured in one sample

X2 = concentration of the same metal measured during replicate analysis

θ = arithmetic mean of X1 and X2.

4.3.4.2 MDLs

MDLs are determined according to the procedures of 40 CFR Part 136 Appendix B using spiked and digested filters fortified at a concentration of two to five times the estimated MDL. The minimum MDLs that must be achieved are shown in Table 4.3-2.

Table 4.3-2. MDLs for EPA Compendium Method IO-3.5

Compound	(ng/filter)
antimony	20
arsenic	50
beryllium	15
cadmium	25
chromium (total)	50
cobalt	50
lead	20
manganese	100
nickel	50
selenium	150
mercury	0.2

MDLs are established for all analytes by preparing a filter strip fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, at least seven replicates of a spiked filter strip are used, and each is processed through the entire analytical method. The MDL is calculated as follows:

$$MDL = (t) \times (S) \qquad (4.3\text{-}2)$$

Where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n - 1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analysis.

MDLs must be determined prior to initiation of sample analysis and whenever a significant change in background or instrument response is expected (e.g., detector change).

Linear calibration ranges are a function of the linear range of the detector. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Damage to the detector should be avoided during this process. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every year or whenever a significant change in instrument response is expected (e.g., detector change).

4.3.4.3 QC Specifications

QC specifications (QCS) for ICP/MS analysis are summarized in Table 4.3-3.

Table 4.3-3. QCS for ICP/MS Analysis

QC Procedure	Typical Frequency	Criteria
Initial calibration (IC)	At the beginning of the analysis	None
Initial calibration verification (ICV) using the QCS	Immediately after initial calibration	90 - 110% of the actual concentration
Initial calibration blank (ICB)	Immediately after initial calibration verification	Must be less than MDLs
High standard verification (HSV)	Following the initial calibration blank analysis	95 - 105% of the actual concentration

(Continued)

Table 4.3-3. (Continued)

QC Procedure	Typical Frequency	Criteria
Interference check standard (ICS)	Following the high standard verification every 8 hours and at the end of a run	80 - 120% of the actual concentration
Continuing calibration verification (CCV)	Analyzed before the first sample, after every 10 samples and at the end of the run	90 - 110% of the actual concentration
Continuing clarification blanks (CCBs)	Analyzed following each continuing calibration verification	Must be less than MDLs
Reagent blank (RB) or Method blank (MB)	1 per 20 samples, a minimum of 1 per batch	Must be less than MDLs
Laboratory control spike (LCS) or LFB	1 per 20 samples, a minimum of 1 per batch	80 - 120% recovery, with the exception of Ag and Sb
Matrix spike (MS)	1 per 20 samples per sample batch	Percent recovery of 75 - 125%
Serial dilution	1 per sample batch	90 - 110% of undiluted sample
Sample dilution	Dilute sample beneath the upper calibration limit but no lower than at least 5 times the MDL	As needed

4.3.5 Instrument Operating Conditions

Example instrument operating conditions for the ICP/MS analysis are presented below. Exact procedures/conditions will be established by individual laboratories for specific instruments.

Instrument	*VG PlasmaQuad Type I*
Plasma forward power	1.35 kW
Coolant flow rate	13.5 Lpm
Auxiliary flow rate	0.6 Lpm
Nebulizer flow rate	0.78 Lpm
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15°C

Data Acquisition

Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 microsecond
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 min/sample

4.3.6 Analysis Procedure

Samples are received from the preparation laboratory in centrifuge tubes. The metals are contained in a mixture of nitric and hydrochloric acids. For every new or unusual matrix, a semi-quantitative analysis should be performed to screen for high element concentrations. Information gained from this procedure may be used to prevent potential damage to the detector during sample analysis and to identify elements that may be higher than the linear range. Matrix screening may be carried out by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards to prevent bias. The analyst should also follow the listed steps below:

1. The instrument operating configuration is initiated by tuning and calibrating the instrument for the analytes of interest.

2. Instrument software procedures are established for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Any integrations considered to be statistical outliers are discarded, and the average of the integrations is used for data reporting.

3. All masses that might affect data quality are monitored during the analysis. At a minimum, IS masses must be monitored in the same scan used for the collection of the data. This information should be used to correct the data for identified interferences.

4. The rinse blank is used to flush the system between samples. Sufficient time must be allowed to remove traces of the previous sample (a minimum of 1 min).
5. Samples are aspirated for 30 seconds prior to the collection of data.

6. Samples having concentrations higher than the established linear dynamic range must be diluted into range and reanalyzed. First, the sample is analyzed for trace elements; the detector is protected from the high concentration elements, if necessary, by selecting appropriate scanning windows. Then the sample is diluted to determine the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided QC data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

Sample data must be reported in units of ng/m^3. All calculated values are reported, with metal concentrations below the determined MDL appropriately flagged. For data values less than 10, two significant figures are used to report element concentrations. For data values greater than or equal to 10, three significant figures are used. Reported values should be calibration blank subtracted.

Data values for instrument drift or sample-matrix-induced interferences are corrected by applying internal standardization. Corrections for characterized spectral interferences should be applied to the data. The chloride ion is a common constituent of environmental samples, and because hydrochloric acid is added during filter extraction, chloride interference corrections should be made on all samples.

If a metal has more than one monitored isotope, the calculated concentration is examined for each isotope, or the isotope ratios, to detect a possible spectral interference. Both primary and secondary isotopes should be considered when evaluating the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes. Differences between the results do not, therefore, necessarily indicate a problem with data calculated for the primary isotopes.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

4.3.7 Hexavalent Chromium Sampling and Analysis

Chromium is a natural constituent of the earth's crust and present in several oxidation states. Trivalent chromium is naturally occurring and environmentally pervasive as a trace element in man and animals. Hexavalent chromium is anthropogenic and arises from a number of commercial and industrial sources. Hexavalent chromium readily penetrates biological membranes and has been identified as a toxic and cancer-causing substance; the element is a known inhalation irritant and is associated with respiratory cancer.

Because of the high level of toxicity of hexavalent chromium, speciation of chromium must be performed to identify the hexavalent state. Separate sampling and analytical methods are required for measuring hexavalent chromium. The analysis of hexavalent chromium is essential when there is a public concern and high probability for the detection of this element in an urban area.

Hexavalent chromium can be a concern for some of the nation's urban areas, especially if the total chromium value is over the limits that the individual states set. Hexavalent chromium cannot be detected by EPA Compendium Method IO-3.5.[7] Separate sample collection and analysis methods using specially prepared filter media and ion chromatography (IC) are used to detect hexavalent chromium.

4.3.7.1 Hexavalent Chromium Sample Collection

Hexavalent chromium samples are collected by pulling ambient air through prepared filters at a known flow rate for a period of 24 hours.

Filter Preparation

Whatman #41 37-mm cellulose filters are used for the collection of hexavalent chromium; the filters must be handled in the cleanest possible laboratory environment. Consequently, filter

preparation must be performed in a nitrogen-purged glove box to minimize the potential for contamination. Approximately 20 cellulose filters at a time are placed in sodium carbonate impregnating solution in a petri dish and soaked for 20 min. The filters are removed from the impregnating solution and allowed to dry on a plastic net or drying rack in a nitrogen-purged glove box. Individual prepared filters are placed in separate petri dishes labeled with preparation date, initials of the preparer, and a unique lot number. The filters in their petri dishes are stored in the freezer until used for sampling.

Sample Collection Procedures

The specially prepared filters are stored in a freezer in labeled and sealed containers until they are ready for use. Because the prepared filter media can potentially collect hexavalent chromium passively from the atmosphere, the field collection event should be set up as close to the actual starting time as possible, and sample recovery should be performed as soon after completion of collection as possible. The hexavalent chromium sampling system is designed to automatically perform a 24-hour filter collection and is automated using a digital timer to initiate sample collection at a flow rate of 9 Lpm. At the end of the 24-hour collection period, the filter is removed from the sampler, returned to the labeled container, placed in a sealable plastic bag and either placed in a freezer or placed in a cooler for shipment to the laboratory for analysis.

4.3.7.2 Hexavalent Chromium Analytical Method

To perform analysis of exposed filters for hexavalent chromium, an ion chromatograph consisting of the following modular units is required:

- Gradient pump;
- Reagent delivery module;
- Variable wavelength detector;
- Automated sampler.

The analysis is performed by IC with postcolumn derivatization using diphenylcarbohydrazide. In the analysis, hexavalent chromium exists as chromate due to the near-neutral pH of the eluent. After separation through the column, hexavalent chromium forms a specific derivative complex with the diphenylcarbohydrazide, which is detected at 520 nm. Due to the oxidation/reduction and the interconversion of trivalent chromium and hexavalent chromium, filter extraction should be performed immediately prior to analysis. Hexavalent chromium concentrations have been shown to increase significantly with time due to reaction with interfering substances present in the air. The IC must be equilibrated and ready for analysis before the samples are prepared. After calibration is performed, a control check standard, water blank, filter blank and filter spike should be analyzed. The ambient samples are analyzed along with a check standard after every tenth sample.

Hexavalent chromium stock standards are recommended to be NIST certified.

Samples, filter blanks, method blanks, and filter spikes are prepared by placing the proper filter into a Teflon test tube, adding deionized water and capping the test tube tightly. A rack of test tubes is placed in a sonicator bath at room temperature for three hours and removed. Approximately 5 mL of the extracted solution is placed in an IC autosampler vial. For replicate samples, sample aliquots are transferred into two separate vials. Extracts are refrigerated until all analyses are completed, nominally within 24 hours of extraction.

4.3.7.3 Method Detection Limits

MDLs are based on procedures from 40 CFR Part 136 Appendix B. The minimum MDL that must be achieved for hexavalent chromium is 0.12 ng/mL. Variation from laboratory to laboratory can be due to the chemist's experience with the method and instrument. Comparability of data reported is essential at the low levels of hexavalent chromium detected in the ambient air. MDLs are determined by performing analysis of 7 - 10 spiked filters and applying the principles of the procedure to the sample set. Filters are spiked at a level of two to five times the estimated MDL.

4.3.7.4 QC Considerations

If the calibration linearity is less than 0.950 expressed as the correlation coefficient, the standards should be reanalyzed and/or reprepared. Control standards should be analyzed at the beginning and end of each analysis set. Check standards should be analyzed after every tenth sample. The limits for both control and check standards should be ±20% of the target concentration. If one or more check standards are not within limits, the affected samples should be reanalyzed until all of the check standards are in control. To test for contamination in either the deionized water or on the cellulose filters, filter and water blanks are prepared along with the samples and analyzed at the beginning of the sample set.

Spikes are prepared by spiking unexposed impregnated filters with a standard hexavalent chromium solution. These spikes are prepared with each sample set and analyzed after the filter blank. The recommended filter spike calculation concentration is 1.0 ng/mL. The spike recovery limit is ±20%.

4.4 OVERVIEW OF SEMIVOLATILE ORGANIC COMPOUNDS MEASUREMENT

EPA Compendium Method TO-13A[10] (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-13ar.pdf) sample collection procedures will be used to collect samples and EPA SW-846 Method 8270C[11] (http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf) will be used to analyze samples for SVOCs in ambient air as required for the NATTS Program. Method 8270C analytical procedures paired with Method 3540C[12] (Soxhlet extraction) (http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3540c.pdf) are used to prepare and analyze ambient air field samples collected on a filter and XAD-2® sorbent. In Method 8270C analysis, the filter and the sorbent are extracted together because of the problem of postcollection volatilization that prohibits accurate determination of the distribution of SVOCs between the gaseous and particulate phase.

4.4.1 Sampling Procedures and Issues Associated with EPA Compendium Method TO-13A[10]

Sample collection for quantitative determination of SVOCs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a sampling cartridge containing 40 grams (g) of XAD-2® across a 24-hour collection period.

4.4.1.1 Sampling Equipment and Materials

Materials and equipment used to conduct SVOC sampling for EPA Compendium Method TO-13A are presented below.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate through the filter/XAD-2® sampling cartridge that will yield a total sample volume greater than 180 standard cubic meters (scm) across a 24-hour duration.

- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the sampler flow path and characterizing the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates, or a variable orifice device.

- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.

- XAD-2® Resin. XAD-2® resin is a styrene-divinylbenzene polymer. Cleaning and preparation of XAD-2® is discussed in detail in Sections 4.4.2.3 and 4.4.2.4, respectively. The amount of XAD-2® used for each sampling episode is 40 g.

- Glass sample cartridge. The cartridge used to contain/secure the XAD-2® resin during sample collection is comprised of a thick-walled glass tube outfitted with a coarse quartz frit at the outlet end. The frit is used to ensure that the resin is not pulled out of the sampling module by the sampling system during sample collection.

4.4.1.2 Sample Collection Procedures

The sampler should be located in an unobstructed area at least 2 m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 - 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head.

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A.[10] The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of each individual sampler. Note that the Magnehelic readings associated with use of a glass frit XAD-2® cartridge will be significantly lower than the readings typically achieved using polyurethane foam (PUF)

cartridges because the glass frit material is more restrictive of flow. Readings in the range of 8 - 30 in. H_2O for glass frit XAD-2® cartridges are not unusal.

Sample Collection

The prepared XAD-2® cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the XAD-2®. The XAD-2® cartridge is then removed from the high volume sampler and transported to the laboratory.

4.4.2 Analysis Procedures and Issues

Table 4.4-1 presents the SVOCs that can be measured using EPA Compendium Method TO-13A[10] (with XAD-2® as the collection medium) and GC/MS as the analytical technique for the NATTS Program.

Table 4.4-1. SVOCs Measured for the NATTS Program Using the Procedures of EPA Compendium Method TO-13A

Compound	CAS Number	Compound	CAS Number
N-nitrosodimethylamine	62-75-9	3-nitroaniline	99-09-2
ethyl methane sulfonate	62-50-0	acenaphthylene	208-96-8
2-picoline (2-methylpyridine)	109-06-8	2,4-dinitrophenol	51-28-5
2-fluorophenol (surr)	367-12-4	4-nitrophenol	100-02-7
			(Continued)
Compound	**CAS Number**	**Compound**	**CAS Number**

methyl methane sulfonate	66-27-3	acenaphthene-d_{10} (IS)	
phenol-d_5 (surr)		acenaphthene	83-32-9
phenol	108-95-2	2,4-dinitrotoluene	121-14-2
bis(2-chloroethyl) ether	111-44-4	2-naphthylamine	91-59-8
aniline	62-53-3	dibenzofuran	132-64-9
2-chlorophenol	95-57-8	pentachlorobenzene	608-93-5
1,3-dichlorobenzene	541-73-1	1-naphthylamine	134-32-7
1,4-dichlorobenzene-d_4 (IS)		diethyl phthalate	84-66-2
1,4-dichlorobenzene	106-46-7	2,3,4,6-tetrachlorophenol	58-90-2
benzyl alcohol	100-51-6	4-nitroaniline	100-01-6
o-cresol (2-methylphenol)	95-48-7	4-chlorophenyl phenyl ether	7005-72-3
1,2-dichlorobenzene	95-50-1	fluorene	86-73-2
bis(2-chloroisopropyl) ether	108-60-1	4,6-dinitro-2-methylphenol	534-52-1
p-cresol (4-methylphenol)	106-44-5	diphenylamine	122-39-4
N-nitrosodi-*n*-propylamine	621-64-7	azobenzene	103-33-3
hexachloroethane	67-72-1	phenacetin	62-44-2
acetophenone	98-86-2	4-bromophenyl phenyl ether	101-55-3
nitrobenzene-d_5 (surr)		4-aminobiphenyl	92-67-1
nitrobenzene	98-95-3	hexachlorobenzene	118-74-1
N-nitrosopiperidine	100-75-4	pronamide	23950-58-5
isophorone	78-59-1	pentachlorophenol	87-86-5
2-nitrophenol	88-75-5	phenanthrene-d_{10} (IS)	
2,4-dimethylphenol	105-67-9	phenanthrene	85-01-8
bis(2-chloroethoxy) methane	111-91-1	anthracene	120-12-7
2,4-dichlorophenol	120-83-2	carbazole	86-74-8
", "-dimethylphenethylamine	122-09-8	di-*n*-butyl phthalate	84-74-2
4-chloroaniline	106-47-8	benzidine	92-87-5
1,2,4-trichlorobenzene	120-82-1	fluoranthene	206-44-0
naphthalene-d_8 (IS)		pyrene	129-00-0
naphthalene	91-20-3	2,4,6-tribromophenol (surr)	118-79-6
2,6-dichlorophenol	87-65-0	4-dimethylaminoazobenzene	60-11-7

(Continued)

Table 4.4-1. (Continued)

Compound	CAS Number	Compound	CAS Number
hexachlorobutadiene	87-68-3	butyl benzyl phthalate	85-68-7
1,4-phenylenediamine	106-50-3	3,3'-dichlorobenzidine	91-94-1
N-nitrosodi-*n*-butylamine	924-16-3	*bis*(2-ethylhexyl) phthalate	117-81-7
4-chloro-3-methylphenol	59-50-7	benzo(a)anthracene	56-55-3
2-methylnaphthalene	91-57-6	chrysene-d_{12} (IS)	
1,2,4,5-tetrachlorobenzene	95-94-3	chrysene	218-01-9
2,4,6-trichlorophenol	88-06-2	di-*n*-octyl phthalate	117-84-0
2-fluorobiphenyl (surr)	321-60-8	7,12-dimethylbenz(a)anthracene	57-97-6
hexachlorocyclopentadiene	77-47-4	benzo(b)fluoranthene	205-99-2
2,4,5-trichlorophenol	95-95-4	benzo(k)fluoranthene	207-08-9
2-nitroaniline	88-74-4	terphenyl-d_{14} (surr)	
2-chloronaphthalene	91-58-7	benzo(a)pyrene	50-32-8
1-chloronaphthalene	90-13-1	indeno(1,2,3-cd)pyrene	193-39-5
dimethyl phthalate	131-11-3	dibenz(a,h)anthracene	53-70-3
2,6-dinitrotoluene	606-20-2	benzo(g,h,i)perylene	191-24-2

surr = surrogate compound

4.4.2.1 Interferences

Method interferences may arise from contaminants in solvents, reagents, glassware, sorbent and other materials used in sample preparation that produce distinct peaks in the chromatogram or from mixtures of compounds that produce an elevated baseline in the chromatogram. All materials used in sampling and in preparation of samples must be free from contamination. Proper cleaning of XAD-2® is especially critical.

Contamination by carryover occurs when a high concentration sample is followed by a low concentration sample. Whenever an unusually concentrated sample is encountered, analysis of solvent or of a blank should follow to demonstrate that cross-contamination is not occurring.

4.4.2.2 Preparation of Reagents and Materials

- Glassware. Glassware must be carefully cleaned before use. Glassware should be cleaned as soon as possible after use by rinsing with the last solvent that was used and then rinsing in high-purity methylene chloride. After these rinses, glassware should be washed carefully using laboratory detergent and hot water, rinsed with tap water, then rinsed with reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for four hours. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent contamination. Glassware should be stored inverted or capped with solvent-rinsed aluminum foil. **Note: Volumetric glassware must not be heated in a muffle furnace.** Volumetric glassware should be rinsed with chromatographic-grade methylene chloride.

- Solvents and materials. Solvents used in the preparation or extraction of the sorbent (methanol, methylene chloride) should be high purity and glass distilled. Boiling chips should be solvent extracted and/or heated in a muffle furnace at 450°C for two hours. Sodium sulfate (anhydrous, granular, ACS grade) should be heated at 400°C in a shallow tray in a muffle furnace for two hours. Chromatographic-grade stainless steel tubing and stainless steel fittings should be used for all connections in the gas chromatograph. Quartz filters (110 mm) should be extracted with methylene chloride, baked at 400°C for five hours prior to use, then stored in a clean container for shipment to and from the field.

4.4.2.3 Cleaning of XAD-2®

The procedure below for cleaning XAD-2® is designed to meet EPA-recommended criteria for cleanliness. Although some forms of "clean" resin are commercially available, laboratory cleaning has proven to be a cost-effective, high quality procedure for obtaining very clean resin usable for ambient air sampling applications. The procedure for cleaning XAD-2® is derived from the EPA Level 1 Procedures Manual[13]. The original methodology has been improved to provide a reproducible procedure for preparing sorbent material that will yield sorbent that is clean enough for low level organic compound collection and analysis. The complete cleaning cycle requires approximately five working days to complete (exclusive of quality control analyses). The typical background or blank total organic concentrations from XAD-2® prepared by this procedure are on the order of 1 : g per gram of sorbent medium. Individual analytes are typically below MDLs. The following steps are utilized to clean and prepare the sorbent for sampling:

— XAD-2® resin is obtained from the supplier or recycled from prior use (recycled material is preferred). Recycled and recleaned resin usually contains less organic contamination and is preferred over raw material directly from the manufacturer.

— The resin is washed with water if new from the supplier. The resin is soaked in tap water at room temperature for three days (or longer) in a clean plastic, glass, or metal vessel large enough to contain the amount of resin to be cleaned. The water and fine particles are decanted by carefully pouring, and fresh water is added. The resin is soaked with fresh tap water for another three days. The water and fine particles are again decanted, after which the new XAD-2® is cleaned in the same manner as the used XAD-2®.

— Recycled or used resin is loaded directly into a large extractor for solvent cleaning. The entire cleaning process is done "wet"; final drying takes place only at the end of the process. An extractor capable of holding 900 g of resin is used to extract the resin using sequential 18-hour extractions with methanol, methylene chloride, and a final extraction with fresh methylene chloride. The solvent is drained between steps, and the extractor is prerinsed with the solvent to be used in the next step. The extractor operates like a Soxhlet extractor with distilled solvent constantly passing over the XAD-2®.

— After the final extraction, the methylene chloride is drained and the extractor body is removed to a hood where the resin is dried. Drying is accomplished using a gentle stream of nitrogen passed through the bottom of the extractor body. Very clean nitrogen is delivered through a heat exchanger attached to the liquid output of a liquid nitrogen tank.

— A methylene chloride extract of approximately 40 g of the resin (approximately 300 mL) is concentrated to 1 mL and analyzed by Method 8270C as a QC check of the cleaned material.

— The jar of dry XAD-2® that has met QC criteria (no Method 8270C analytes observed at levels above the MDL) is labeled with a laboratory identification and stored in a clean, solvent-free cabinet for use in sampling activities. The cleaned dried resin will remain usable for 2 - 3 weeks stored at room temperature. Longer storage times are possible if the material is refrigerated, but a blank sample must be checked before resin stored for longer than three weeks may be considered usable for field sampling.

— A 2-L glass bottle is filled nearly full with XAD-2®, wet or as a slurry or dry. Sufficient clean methanol is transferred to the bottle to just cover the XAD-2®, and the resin is allowed to soak for three days. The methanol and fine particles are decanted. The bottle is again filled with methanol and sealed (screw cap and Teflon tape). The XAD-2® is allowed to soak indefinitely in the methanol until the

resin is needed for sampling; the resin can be dried immediately before it is needed.

Contaminants may appear in the resin and will cause the cleaned resin to fail the QC test performed at the end of the cleaning procedure. Common resin contaminants include inorganic salts and preservatives often present in new resin as received from the supplier (careful rinsing with water at the first step will rinse these materials from the resin) and hydrocarbon contaminants. Dirty resin often contains hydrocarbon contamination that appears in the C_8 - C_{12} range in the GC/MS analysis. This interference is eliminated by sufficiently cleaning the resin with the recommended solvent extractions. Some analytical interferences of contaminants appear in the resin after storage. These contaminants may cause the cleaned resin to fail the QC requirements for the analytical method. Contaminants may originate from both external contamination or oxidation and from internal "bleeding" of entrained chemicals from very small or inaccessible pores in the resin. Subsequent recleaning and reuse reduce the internal contributions to the blank level during storage. Contaminant levels may also increase if XAD-2® is exposed to high concentrations of oxidizing agents such as ozone or oxides of nitrogen. In an oxidizing matrix, oxidation or decomposition products of XAD-2®, such as naphthalene, benzoic acid, benzaldehyde, carboxylic acids and aldehydes, will be observed. Sufficiently high levels of oxides of nitrogen (NO_x) (percentage levels) can cause destruction of the resin itself.

4.4.2.4 Preparation of a Sampling Cartridge

Cleaned XAD-2® (approximately 40 g) that has passed Method 8270C acceptance criteria for cleanliness is loaded into a glass thimble with an extra coarse glass frit. The glass thimble is 55 mm in diameter and measures 100 mm from the frit to the top of the thimble. Clean thimbles are rinsed with methylene chloride, tared and dried for use. The thimble filled with XAD-2® is wrapped tightly with aluminum foil that has been rinsed with methylene chloride and oven dried, wrapped securely in bubble wrap and placed in a plastic jar for shipment to the field. Multiple filled thimbles are shipped to the field as a batch, together with 110-mm quartz filters that have been precleaned with methylene chloride and placed in individual sealable plastic bags with chain

of custody documentation. The XAD-2® modules and filters are shipped in coolers over Blue Ice to keep them cool in shipment.

4.4.2.5 Reagents

Any water used must be organic-free reagent water. Standard solutions may be prepared from pure standard materials or purchased as certified solutions. Stock standard solutions are considered stable for one year but must be replaced whenever comparison with QC check samples indicates a problem.

The ISs used for Method 8270C are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. These compounds may be purchased as pure standard materials or purchased as a certified solution. Stock standard solutions are considered stable for one year but must be replaced whenever comparison with QC check samples indicates a problem.

A tuning/column performance solution containing 50 ng/ : L each of DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine may be prepared from pure standards or purchased as a certified solution. This solution is used to establish/verify the instrument tune, the inertness of the injector port and column performance. The tuning/column performance solution should be stored at -10°C when not in use. Degradation of DDT to DDE and DDD should not exceed 20%, benzidine and pentachlorophenol should be present at their normal responses and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injector liner may need to be replaced and/or column maintenance may need to be performed.

A minimum of five calibration standards should be prepared at five different concentrations, with at least one of the concentrations corresponding to a sample concentration near the MDL. The highest concentration calibration standard must not exceed the linear range of the instrument. All of the compounds of interest should be included in the calibration standards; the laboratory may not report a quantitative result for a compound not included in the calibration

standards. The calibration standards should be stored at a temperature #-10°C and should be freshly prepared at least once a year (sooner if check standards indicate a problem).

The surrogate compounds for Method 8270C are phenol-d_6, 2-fluorophenol, 2,4,6-tribromo-phenol, nitrobenzene-d_5, 2-fluorobiphenyl, and *p*-terphenyl-d_{14}. Surrogate compounds are spiked into the sample immediately before extraction. The surrogate compound solution may be prepared from pure standards or purchased as a certified solution.

A matrix spike is typically not performed for Method 8270C analysis of ambient air samples. However, a method spike (or LCS) is prepared by spiking clean XAD-2® with a solution containing all of the compounds of interest at levels comparable to those expected in the field samples. Surrogate compounds are also added to the method spike.

4.4.2.6 Analytical Equipment

A GC/MS with a data system and autosampler is used in the analysis of calibration samples, field samples and QC samples. The GC must be equipped for temperature programming, splitless/split injection and a capillary column. A fused silica DB-5 column (30-m × 0.32-mm i.d.) cross-linked 5% phenyl methyl silicone, 1.0-:m film thickness (or equivalent) may be used. The GC is coupled directly to the ion source of the mass spectrometer. The mass spectrometer must be capable of scanning from 35 - 500 amu every second or less, using an electron energy of 70 electron volts (eV) (nominal) to produce electron ionization mass spectra. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets the criteria in Table 4.4-2 when 1 microliter (:L) of the GC/MS tuning standard (50 ng DFTPP on-column) is injected through the GC.

Table 4.4-2. DFTPP: Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present but <mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

4.4.2.7 Sample Extraction, Concentration and Cleanup

The XAD-2® sampling module and filter are carefully packed with padding, placed in a cooler with Blue Ice and returned to the laboratory from the field. Field samples should be stored and shipped chilled (<4°C) using Blue Ice until the samples are received at the analytical laboratory. After receipt at the analytical laboratory, the samples should be refrigerated at #4°C. Samples should be extracted within 14 days after sampling; extracts should be analyzed within 45 days after extraction. The sorbent and filter are extracted together. Extraction procedures follow Method 3540C (Soxhlet extraction). Sample extracts are concentrated to a final volume of 1 mL and stored at -10°C protected from light in sealed vials equipped with an unpierced PTFE-lined septum.

A Soxhlet extraction is performed using approximately 700 mL of methylene chloride, with the sorbent and filter extracted together in the Soxhlet extractor; the extractor should reflux for 18 hours at a rate of at least 3 cycles per hour. Prior to extraction, the laboratory surrogate standards are spiked into each sample and blank at a level of 1 : g/mL. The recovery of the laboratory

surrogate is used to monitor for matrix effects or errors in sample preparation and should be in the range of 60 - 120%. The extractor is allowed to cool then disassembled. The extract is dried by passing it through a drying column containing ~ 10 g of cleaned anhydrous sodium sulfate, then concentrated using a Kuderna-Danish concentration apparatus with nitrogen blow-down to a final volume of 1.0 mL. The extract is transferred to a Teflon-sealed, screw cap amber vial and stored at 4 ± 2°C until analysis.

To perform a matrix spike analysis, a specific field sample must be taken and designated for this purpose. Matrix spikes are generally not performed for ambient air samples. An LCS in which all of the analytes are spiked onto a clean sorbent matrix and recovered in the laboratory is performed to monitor matrix effects.

If the extract is cloudy, the extract may be purified by solid phase extraction using activated silica gel. If the sample matrix is clean, sample cleanup is not needed. The extract is cleaned up using a succession of solvents with approximately 10 g of cleaned activated silica gel, according to the procedures of EPA Compendium Method TO-13A.[10] The extract eluted from the silica gel cleanup column is concentrated to < 5 mL using a Kuderna-Danish concentrator, then to a final volume of 1 mL using nitrogen blow-down.

4.4.2.8 Initial Calibration

The GC/MS system must be hardware tuned to meet tuning criteria (Table 4.4-2) according to the procedures recommended in Method 8270C using a 50-ng injection of DFTPP; no analyses may begin until tuning criteria are met. All subsequent standards, samples, LCS, method spikes, and blanks associated with a specific DFTPP analysis must use the identical mass spectrometer instrument conditions.

The ISs selected above have been chosen to cover the chromatographic elution times of the compounds to be measured for the NATTS Program and should permit the compounds of interest

in the chromatogram to have retention times of 0.80 - 1.20 relative to one of the ISs. The typical quantitation scheme for Method 8270C analytes is shown in Table 4.4-3. The primary ion of both the IS and the compound of interest should be used to perform quantitative calculations, unless analytical interferences are noted. If interferences are observed, the next most intense ion of the mass spectrum should be used as the quantitation ion. Note that secondary ion quantitation is permissible ONLY if analytical interferences are encountered; secondary ion quantitation may not be used if the primary ion is saturated because the quantitative calculations performed for a compound that is saturated will be biased significantly low.

Table 4.4-3. Quantitation Scheme for Semivolatile Organic Compounds According to Method 8270

1,4-dichlorobenzene-d_4 (IS)	**naphthalene-d_8 (IS)**	**acenaphthene-d_{10} (IS)**
Compounds to be quantitated against each IS above		
aniline	acetophenone	acenaphthene
benzyl alcohol	benzoic acid	acenaphthylene
bis(2-chloroethyl) ether	*bis*(2-chloroethoxy) methane	1-chloronaphthalene
bis(2-chloroisopropyl) ether	4-chloroaniline	2-chloronaphthalene
2-chlorophenol	4-chloro-3-methylphenol	4-chlorophenyl phenyl ether
1,3-dichlorobenzene	2,4-dichlorophenol	dibenzofuran
1,4-dichlorobenzene	2,6-dichlorophenol	diethyl phthalate
1,2-dichlorobenzene	",-dimethylphenethylamine	dimethyl phthalate
ethyl methanesulfonate	2,4-dimethylphenol	2,4-dinitrophenol
2-fluorophenol (surrogate)	hexachlorobutadiene	2,4-dinitrotoluene
hexachloroethane	isophorone	2,6-dinitrotoluene
methyl methanesulfonate	2-methylnaphthalene	fluorene
2-methylphenol (*o*-cresol)	naphthalene	2-fluorobiphenyl (surrogate)

(Continued)

Table 4.4-3. (Continued)

1,4-dichlorobenzene-d_4 (IS)	**naphthalene-d_8 (IS)**	**acenaphthene-d_{10} (IS)**
Compounds to be quantitated against each IS above		
4-methylphenol (*p*-cresol)	nitrobenzene	hexachlorocyclopentadiene
N-nitrosodimethylamine	nitrobenzene-d_8 (surrogate)	1-naphthylamine
N-nitrosodi-*n*-propylamine	2-nitrophenol	2-naphthylamine
phenol	N-nitrosodi-*n*-butylamine	2-nitroaniline
phenol-d_6 (surrogate)	N-nitrosopiperidine	3-nitroaniline
2-picoline	1,2,4-trichlorobenzene	4-nitroaniline
		4-nitrophenol
		pentachlorobenzene
		1,2,4,5-tetrachlorobenzene
		2,3,4,6-tetrachlorophenol
		2,4,6-tribromophenol (surrogate)
		2,4,6-trichlorophenol
		2,4,5-trichlorophenol
phenanthrene-d_{10} (IS)	**chrysene-d_{12} (IS)**	**perylene-d_{12} (IS)**
4-aminobiphenyl	benzidine	benzo(b)fluoranthene
anthracene	benzo(a)anthracene	benzo(k)fluoranthene
4-bromophenyl phenyl ether	*bis*(2-ethylhexyl) phthalate	benzo(g,h,i)perylene
di-*n*-butyl phthalate	butyl benzyl phthalate	benzo(a)pyrene
4,6-dinitro-2-methylphenol	chrysene	dibenz(a,j)acridine
diphenylamine	3,3'-dichlorobenzidine	dibenz(a,h)anthracene
fluoranthene	*p*-dimethylaminoazobenzene	
hexachlorobenzene	pyrene	
N-nitrosodiphenylamine	terphenyl-d_{14} (surrogate)	
pentachlorophenol	7,12-dimethylbenz(a)anthracene	
pentachloronitrobenzene	di-*n*-octyl phthalate	
phenacetin	indeno(1,2,3-cd)pyrene	
phenanthrene	3-methylcholanthrene	
pronamide		

An injection of 1 :L of each calibration standard (calibration range 20, 50, 80, 120, 160 :g/mL) containing ISs is analyzed and response factors for each compound of interest relative to the nearest eluting ISs are calculated according to Equation 4.4-1.

$$RF = (A_s \times C_{is}) / (A_{is} \times C_s) \quad (4.4\text{-}1)$$

Where:

A_s = area of the quantitation ion of the compound of interest

A_{is} = area of the quantitation ion of the IS

C_s = concentration of the compound of interest, :g/mL

C_{is} = concentration of the Internal Standard, :g/mL.

A system performance check must be performed to ensure that minimum average response factors for a specific set of compounds are obtained before the calibration curve may be used. For SVOCs, the system performance check compounds are:

- N-nitrosodi-*n*-propylamine;
- hexachlorocyclopentadiene;
- 2,4-dinitrophenol; and
- 4-nitrophenol.

The minimum acceptable average response factor for these compounds is 0.050. These compounds typically have low response factors (0.1 - 0.2), and the compound responses tend to decrease as the chromatographic system deteriorates or the standards degrade. These compounds are usually the first to show poor system performance. If the minimum average response factor requirement is not met, the GC/MS system must be evaluated, and corrective action must be taken before samples are analyzed. Possible problems include degradation of standards, injector or column contamination or active sites in the column or in the chromatographic system. The problem must be corrected and the IC must be repeated.

The calibration check compounds are used to evaluate the calibration and the analytical system: high variability in the response factors for these compounds may be indicative of analytical system leaks or reactive sites on the chromatographic column. The calibration check compounds are shown in Table 4.4-4.

Table 4.4-4. Calibration Check Compounds for Analysis of SVOCs for the NATTS Program

Base/Neutral Compounds	Acid Compounds
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
diphenylamine	phenol
di-*n*-octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

After the IC samples have been analyzed, the mean response factor and standard deviation are calculated, and the RSD is calculated according to Equation 4.4-2.

$$RSD = (SD / \overline{RF}) \times 100 \qquad (4.4\text{-}2)$$

Where:

SD = standard deviation

$\overline{RF}$ = mean response factor.

If the RSD of any calibration check compound is > 30%, the chromatographic system is too reactive for analysis to begin and the injector liner and/or chromatographic column must be cleaned or replaced and the IC must be repeated.

If the RSD of any compound of interest is 15% or less, the RRF is assumed to be constant over the calibration range and the average RRF may be used for quantitation. If the RSD exceeds

15%, plotting and visual inspection of a calibration curve may indicate the source of the analytical problems such as errors in standard preparation, presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

The RRTs for each compound of interest in each calibration standard should agree within 0.06 RRT units.

Calibration Verification

The calibration of the analytical system must be verified every 12 hours. The analysis of DFTPP must be repeated and tuning criteria must be met. If tuning criteria are not met, the analytical system must be retuned and the IC must be repeated. To verify the calibration, a calibration standard at a concentration near the midpoint of the calibration range of the GC/MS must be analyzed. Each system performance check compound must exhibit a minimum response factor of 0.050; if acceptance criteria are not met, the analytical system must be evaluated and corrective action must be taken before analysis is performed. Depending upon the nature of the corrective action, it may be necessary to repeat the IC.

After the system performance check has been performed, the calibration check compounds listed in Table 4.4-4 are used to verify the validity of the IC. Percent difference between the average response factor from the IC and the response factor calculated from the calibration verification sample must be #20% in order for the IC to be considered valid. If the percent difference is >20%, corrective action must be taken before samples can be analyzed. Depending upon the nature of the corrective action, it may be necessary to repeat the IC.

The retention times for each of the ISs in the calibration verification sample must be within ± 30 seconds of the retention time of that IS in the mid-level standard of the most recent IC. If the retention time for any IS changes by more than 30 seconds, analytical system corrections must be made, as required, and reanalysis of samples analyzed while the analytical system was malfunctioning is required.

If the extracted ion current plot area for any IS in the calibration verification standard changes by a factor of two (-50 to +100%) from the comparable value of that IS in the mid-level standard of the most recent IC, analytical system corrections must be made, as required, and reanalysis of samples is required.

4.4.2.9 Analysis of Samples

The sample extracts must warm to room temperature before analysis. Just prior to analysis, the IS is added to the concentrated sample extract in an autosampler vial. A 1-:L sample aliquot of the sample extract is injected into the GC/MS system; this volume should contain 100 ng of base/neutral surrogate compounds and 200 ng of acid surrogate compounds (assuming 100% recovery).

If the response for any primary quantitation ion exceeds the IC range of the analytical system, the sample extract must be diluted and reanalyzed, maintaining the IS level at 40 ng/:L.

Qualitative Analysis

The ID of compounds of interest using Method 8270C is based on comparison of retention times with standards and comparison of the mass spectrum (after background subtraction) with the characteristic ions of a reference mass spectrum generated by the laboratory using the same analytical conditions. The following criteria must be met:

- The characteristic ions of a compound of interest must maximize in the same scan or within one scan of each other;
- The RRT of the sample component is within ±0.06 RRT units of the RRT of the standard component;
- The relative intensities of the characteristic ions agree within 30% with the relative intensities of these ions in the reference spectrum;

- Structural isomers that produce very similar mass spectra may be identified as individual isomers only if they have sufficiently different GC retention times (i.e., 25% valley between the peaks in question). Otherwise, structural isomers should be identified as isomeric pairs; and

- When analytes coelute, ID criteria may be met, but the spectrum will contain extraneous ions contributed by the coeluting compound.

Because Method 8270C is operating in the full-scan mode, a library search of a mass spectrum may be made for tentative ID, if the following criteria are met:

- Relative intensities of major ions in the reference spectrum should be present in the sample spectrum;

- Relative intensities of the major ions should agree within ±20%;

- Molecular ions present in the reference spectrum should be present in the sample spectrum;

- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible contamination or elution of additional compounds; and

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of contamination or coeluting peaks.

Quantitative Analysis

After identification of a compound of interest, quantitative analysis of that compound will be performed on the basis of the integrated abundance of the primary characteristic ion of that compound. If the RSD of the response factor of that compound is #15%, the concentration of that compound in the extract may be determined using the average response factor from the IC curve.

To estimate the concentration of tentatively identified compounds, the same formula is used with a response factor of 1 compared to the nearest eluting IS. The peak areas from the total ion chromatogram should be used. The calculated value should be reported with the qualification that the value is an estimate, with the IS used to determine the estimated concentration.

4.4.3 Determination of MDLs

MDLs that must be achieved for the NATTS Program are presented in Table 4.4-5. MDLs for SVOCs would be most accurately determined by gaseous spiking of the compounds of interest in the field so that the samples would go through the entire sampling and analytical process that field samples experience. This procedure for determination of MDLs is presently not practical, but the closest approximation in the laboratory involves spiking of cleaned certified sorbent so that the samples undergo at least the extraction (and cleanup, if used) and analysis portion of the procedure. The procedures of 40 CFR Part 136 Appendix B are used as a guideline for determination of MDLs. To follow the guidelines of 40 CFR Part 136 Appendix B, the following steps are required:

- Estimate an MDL. This estimate can usually be performed using the calibration standards: if the lowest calibration standard is at a level of 20 ng/:L, the analyst can make some estimate of an MDL from this standard.

- Determine a spiking level for the sorbent matrix. At least seven replicate clean sorbent samples should each be spiked with all of the compounds of interest at a level 2 - 5 times the estimated MDLs. For example, if the estimated MDL is 10 ng/:L, the spiking level for the matrix with a 1-mL final extract volume would be gauged to produce a final concentration of compounds of interest in the range of 20 - 50 ng/:L. Surrogate compounds and ISs are spiked at the same level as they are spiked in field samples.

- Prepare and analyze spiked XAD-2®; calculate MDLs according to the procedure of 40 CFR Part 136 Appendix B. The calculation of the MDLs is based on the standard deviation of the replicate analyses multiplied by the appropriate value of the Student's t corresponding to a 99% confidence level with n - 1 degrees of freedom.

The selection of the spiking level is a critical factor in the success of the determination. The calculation is based on the reproducibility of the measurement. If the spiking level selected is too low, chromatographic peaks will be more difficult to integrate, and the reproducibility of the measurement (and hence the MDLs) will suffer.

Table 4.4-5. MDLs for SVOCs Measured in the NATTS Program[1]

Compound	MDL (:g)	Compound	MDL (:g)
N-nitrosodimethylamine	6.62	acenaphthylene	4.31
pyridine	11.73	2,4-dinitrophenol	8.06
ethyl methanesulfonate	7.07	4-nitrophenol	6.81
2-picoline	32.25	acenaphthene	4.67
N-nitrosomethylethylamine	7.05	2,4-dinitrotoluene	6.53
methyl methanesulfonate	8.07	2-naphthylamine	24.10
N-nitrosodiethylamine	7.24	dibenzofuran	3.29
phenol	8.04	pentachlorobenzene	5.14
pentachloroethane	8.88	1-naphthylamine	24.46
bis(2-chloroethyl) ether	7.03	diethyl phthalate	4.52
aniline	13.16	2,3,4,6-tetrachlorophenol	6.93
2-chlorophenol	7.64	4-nitroaniline	6.04
1,3-dichlorobenzene	5.08	4-chlorophenyl phenyl ether	4.82
1,4-dichlorobenzene	5.72	fluorene	4.21
benzyl alcohol	8.33	5-nitro-*o*-toluidine	5.28
o-cresol (2-methylphenol)	9.14	4,6-dinitro-2-methylphenol	6.48
1,2-dichlorobenzene	6.16	diphenylamine	26.38
bis(2-chloroisopropyl) ether	5.55	azobenzene	6.06
m-, *p*-cresol (3- and 4-methylphenol)	8.43	phenacetin	4.75
N-nitrosopyrrolidine	7.31	diallate	4.70
N-nitrosodi-*n*-propylamine	5.52	4-bromophenyl phenyl ether	6.09
o-toluidine	7.51	4-aminobiphenyl	26.38
hexachloroethane	5.09	hexachlorobenzene	4.63

(Continued)

Table 4.4-5. (Continued)

Compound	MDL (:g)	Compound	MDL (:g)
acetophenone	6.86	pronamide	5.87
nitrobenzene	5.73	pentachlorophenol	7.54
N-nitrosopiperidine	4.84	pentachloronitrobenzene	7.20
isophorone	5.56	phenanthrene	5.62
2-nitrophenol	9.25	dinoseb	6.23
2,4-dimethylphenol	32.77	anthracene	6.16
bis(2-chloroethoxy)methane	6.93	carbazole	5.74
2,4-dichlorophenol	5.66	di-*n*-butyl phthalate	4.71
4-chloroaniline	9.44	benzidine	50.00[2]
1,2,4-trichlorobenzene	5.47	isodrin	4.55
naphthalene	6.86	fluoranthene	3.85
2,6-dichlorophenol	5.66	pyrene	5.38
hexachloropropene	6.49	4-dimethylaminoazobenzene	4.35
hexachlorobutadiene	7.20	chlorobenzilate	3.26
N-nitrosodi-*n*-butylamine	4.97	3,3'-dimethylbenzidine	50.00[2]
4-chloro-3-methylphenol	6.83	butyl benzyl phthalate	5.59
safrole	5.89	2-acetylaminofluorene	3.39
2-methylnaphthalene	5.88	3-methylcholanthrene	6.42
1,2,4,5-tetrachlorobenzene	5.99	3,3'-dichlorobenzidine	7.16
2,4,6-trichlorophenol	4.86	*bis*(2-ethylhexyl) phthalate	4.86
hexachlorocyclopentadiene	10.27	benzo(a)anthracene	3.87
2,4,5-trichlorophenol	6.53	chrysene	5.84
2-nitroaniline	6.40	di-*n*-octyl phthalate	4.34
isosafrole	5.82	7,12-dimethylbenz(a)anthracene	5.56
2-chloronaphthalene	4.09	benzo(b)fluoranthene	6.95
1,4-naphthoquinone	5.81	benzo(k)fluoranthene	5.62
dimethyl phthalate	4.37	benzo(a)pyrene	3.57
1,3-dinitrobenzene	7.54	indeno(1,2,3-cd)pyrene	8.09

(Continued)

Table 4.4-5. (Continued)

Compound	MDL (:g)	Compound	MDL (:g)
2,6-dinitrotoluene	6.63	dibenz(a,h)anthracene	5.13
3-nitroaniline	4.83	benzo(g,h,i)perylene	5.64

[1]MDLs are corrected for recovery from XAD-2®.
[2]Estimated MDL; no recovery observed from XAD-2® at the level at which the sorbent was spiked.
Note: Quantitative data from phenol, cresols, benzyl alcohol, acetophenone, dibenzofuran, and possibly other oxygenated compounds may be biased high because of the potential for oxidation of the XAD-2® by ambient ozone during sampling.

4.4.4 Quality Control

QC measures necessary to evaluate the operation of the GC/MS system include:

- Tuning of the GC/MS system to meet DFTPP criteria initially, with verification of the stability of the DFTPP tune every 12 hours of operation;
- IC of the analytical system to meet acceptance criteria, with acceptable performance of the system performance check compounds and the calibration check compounds;
- Acceptable calibration verification every 12 hours of operation; and
- Acceptable stability of RRTs.

The laboratory must perform an initial demonstration of proficiency by analyzing multiple LCSs at an acceptable level of accuracy and precision. The demonstration of proficiency must be repeated as new staff are trained or when significant changes in laboratory instrumentation are made. The LCS consists of cleaned XAD-2® spiked with the surrogate compounds and the compounds of interest. Successful analysis of the LCS demonstrates that the laboratory can perform the sample preparation and analysis successfully in a clean matrix and can be used to document the effect of the matrix on the collected samples.

The analysis of QC samples including a method blank, method spike, and a LCS for each sample batch. The addition of surrogate compounds to each field sample and QC sample is required.

Each laboratory must evaluate surrogate recovery data from individual samples against the surrogate compound control limits developed by the laboratory. Method 8270C includes surrogate compound recovery limits. The values in Table 4.4-6 were established for surrogate compounds in a field dynamic spiking study for stationary source analysis. These values can serve as an approximate guideline until the laboratory establishes its own control limits.

Table 4.4-6. Surrogate Compound Control Limits for SVOC Analysis Using EPA Compendium Method TO-13A[10]/8270C[11]

Surrogate Compound	Estimated Recovery Control Limits (%)
2-fluorophenol	40 - 100
phenol-d_5	50 - 110
nitrobenzene-d_5	35 - 95
2-fluorobiphenyl	46 - 106
2,4,6-tribromophenol	33 - 101
terphenyl-d_{14}	47 - 112

4.4.5 Resolving Polycyclic Aromatic Hydrocarbons (PAHs) Only—An Alternative Approach

Polycyclic aromatic hydrocarbons (PAHs) make up a subset of the SVOCs presented in Table 4.4-1. There may be situations in which it is desirable to measure only the PAHs. Although the preferred method for collection of semivolatile organic compounds uses XAD-2®, PAHs only can be collected using PUF. However, prior approval from EPA must be obtained before PAH-specific measurements can be applied to the NATTS Program, if required. An organic compound

with a boiling point $100°C is considered an SVOC. Within the category of semivolatile organic compounds, PAHs have received increased attention in recent years in air pollution studies because some of the compounds in this class are highly carcinogenic or mutagenic. Specifically, benzo(a)pyrene has been identified as highly carcinogenic. PAHs are primarily products of incomplete combustion processes from natural sources such as wildfires, from industrial processes, transportation, energy production and use, food preparation, smoking tobacco, and disposal activities such as open trash burning. PAHs generally occur as complex mixtures rather than as single compounds. Benzo(a)pyrene (as well as other PAHs) is bioaccumulative, does not break down easily in the environment and is subject to long-range air transport. To understand human risk and the level of human exposure to benzo(a)pyrene and other PAHs, it is necessary to sample and analyze reliably for these compounds. Current methodology requires sampling ambient air with a quartz fiber filter and a sorbent collection module, with subsequent analysis by high resolution gas chromatography coupled with mass spectrometry. EPA Compendium TO-13A,[10] "Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)," is included in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition (EPA/625/R-96/010b). The complete compendium of methods for ambient air is on-line at www.epa.gov/ttn/amtic/airtox.html ; the specific location of Compendium Method TO-13A is www.epa.gov/ttn/amtic/files/ambient/airtox/to-13arr.pdf .

PAHs encompass a broad range of vapor pressures; the least volatile compounds in the category are present in ambient air substantially distributed between gas and particulate phases. EPA Compendium Method TO-13A[10] sampling methodology permits collection of both phases. However, in the operation of the sampling train, nonvolatile PAHs (PAHs with vapor pressure < 10^{-8} mm Hg) may initially be trapped on the filter but will volatilize to an unknown extent as additional air is pulled through the sampling train: this postcollection volatilization will result in the distribution of the PAHs between the filter and the sorbent[14-19]. Because of this postcollection volatilization of collected compounds, separate analysis of the filter will not accurately reflect the

concentrations of the PAHs originally associated with particles; separate analysis of the sorbent will not provide an accurate measurement of the gas phase. EPA Compendium Method TO-13A[10] therefore requires extraction of the filter and sorbent together in order to provide an accurate measurement of total PAH concentrations in ambient air. Because of the relatively low levels of common PAHs in the environment, the methodology suggests the use of a high volume (0.22 m^3/min) sampling technique to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection by filter media alone. Consequently, this method utilizes both a filter and a backup PUF cartridge, which provides for efficient collection of most PAHs involving three member rings or higher. A further consideration in sampling SVOCs is the potential loss of lighter semivolatile compounds if sampling occurs during elevated temperatures.

Many of the PAHs have been identified as highly carcinogenic. To understand the extent of human exposure to these PAHs, reliable sampling and analytical methods are necessary. The EPA Compendium Method TO-13A[10] is used to sample and analyze common PAHs. The method involves the use of a combination of quartz filter and sorbent cartridge with subsequent analysis by GC/MS detection. The use of GC/MS as the recommended procedure for analysis of the PAHs was influenced by its sensitivity and selectivity, along with its ability to analyze complex samples.

A wide variety of sorbents such as Tenax®, XAD-2® and PUF[19,20] have been used to sample common PAHs. All sorbents have demonstrated high collection efficiency. In general, XAD-2® resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. PUF cartridges, however, are easier to handle in the field and maintain better flow characteristics during sampling. PUF has demonstrated its capability in sampling organochlorine pesticides, polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins but has demonstrated a lower recovery efficiency and storage capability for naphthalene than XAD-2®.

Filters and PUF cartridges are cleaned in solvents and vacuum dried. The filters and PUF cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler. Approximately 300 m^3 of air is drawn through the filter and PUF cartridge using a high volume flow rate air sampler or equivalent. The amount of air sampled through the filter and PUF cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with a blank filter and PUF cartridge and COC forms to the analytical laboratory for analysis.

The filters and PUF cartridges are extracted with the appropriate solvent and prepared to remove potential interferences prior to analysis by GC/MS. The eluent is then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentrations of calibration solutions. Other preparation approaches such as accelerated solvent extraction (ASE) may be used if performance equivalent to standard extraction procedures is demonstrated. ASE is safer than conventional extraction procedures and more economical of solvent.

4.4.5.1 Sampling Apparatus and Procedures

Sample collection for quantitative determination of PAHs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by cartridge containing a PUF plug across a 24-hour collection period.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate of approximately 8 standard cubic feet per minute (scfm) through the filter/PUF plug to obtain a total sample volume greater than 325 scm across a 24-hour duration.
- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the sampler flow path and characterizing the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates or a variable orifice device.

- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.

- PUF plugs. The PUF plug is constructed of the polyether type of PUF with a density of 0.022 g/cm^3. The PUF plug is 3 in. thick and has an outside diameter of approximately 2 3/8 inches, or is approximately 1/8-in. larger in diameter than the opening in the cartridge into which the PUF plug slides.

- Glass sample cartridge. The cartridge used to contain/secure the PUF plug during sample collection is comprised of a thick-walled glass tube outfitted with a stainless steel screen at the outlet end. The cartridge is sized to accomplish a leak-tight fit in the high volume sampler so that all sample air is channeled through the PUF plug.

4.4.5.2 Sample Collection Procedures

The sampler should be located in an unobstructed area at least 2 m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 - 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head. When a new sampler is set up or when the sampler is used at a different location, all areas of the sampling apparatus that contact the sample need to be cleared using triple rinses of reagent-grade hexane contained in Teflon wash bottles. All cleaning and washing should be done in a controlled environment to minimize contamination. Solvent should be allowed to evaporate before the PUF sampling module is loaded into the sampler.

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A.[10] The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding

Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of each sampler.

Sample Collection

The prepared PUF cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the PUF plug. The PUF cartridge is then removed from the high volume sampler and transported to the laboratory.

4.4.6 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all of the procedures involved with the analysis of PAHs using EPA Compendium Method TO-13A.[10]

4.4.6.1 Sample Extraction, Concentration and Cleanup

Field samples should be stored and shipped chilled (<4°C) in coolers using Blue Ice until the samples are received at the analytical laboratory. After receipt at the analytical laboratory, the samples should be refrigerated at #4°C. Samples should be extracted within 7 days after sampling; extracts should be analyzed within 40 days after extraction.

A Soxhlet extraction is performed using approximately 700 mL of 10% diethyl ether in hexane, with the sorbent and filter extracted together in the Soxhlet extractor; the extractor should

reflux for 18 hours at a rate of at least 3 cycles per hour. Prior to extraction the laboratory surrogate standards are spiked into each sample and blank at a level of 1.0 : g/mL. The recovery of the laboratory surrogate is used to monitor for matrix effects or errors in sample preparation and should be in the range of 60 - 120%. The extractor is allowed to cool and is then disassembled. The extract is dried by passing it through a drying column containing ~ 10 g of cleaned anhydrous sodium sulfate and is then concentrated using a Kuderna-Danish concentration apparatus followed by nitrogen blow down to a final volume of 1.0 mL. The extract is transferred to a Teflon-sealed, screw cap amber vial and stored at 4 ± 2°C until analysis.

To perform a matrix spike analysis, a specific field sample must be taken and designated for this purpose. Matrix spikes are generally not performed for ambient air samples. An LCS in which all of the analytes are spiked onto a clean sorbent matrix and recovered in the laboratory is performed to monitor matrix effects.

A cloudy extract may be purified by solid phase extraction using activated silica gel. If the sample matrix is clean, sample cleanup is not needed. The extract is cleaned up using a succession of solvents with approximately 10 g of cleaned activated silica gel, according to the procedures of EPA Compendium Method TO-13A.[10] The extract eluted from the silica gel cleanup column is concentrated to < 5 mL using a Kuderna-Danish concentrator and then to a final volume of 1 mL using a nitrogen blow-down.

4.4.6.2 GC/MS Analysis

The analysis of the sample extract for PAH is accomplished by operation of the GC/MS system in the electron ionization mode (nominal 70 eV), using selected ion monitoring (SIM) to monitor the compounds of interest at the highest possible level of sensitivity. SIM monitors only the specified ions; the ability to characterize other compounds is precluded. The GC/MS is tuned using a 5-ng/ : L solution of DFTPP, but the standard tuning criteria for full-scan mode are irrelevant when SIM procedures are used. Since the masses for the PAHs are between 150 and

300, the mass spectrometer should be tuned to maximize the signal for the DFTPP ions above mass 150 (i.e., the mass spectrometer should be tuned to optimize the signal for masses 198, 275, 365, and 442 while maintaining unit resolution between masses 197, 198, and 199 as well as 441, 442, 443).

A stable tune should be established with the highest possible sensitivity for the high masses. The stability of this tune should be demonstrated every 12 hours.

Analysis of Field Samples by GC/MS

Field samples are extracted, cleaned up if necessary and concentrated to a final volume of 1 mL. All sample extracts are allowed to warm to room temperature before analysis (~ 1 hour). After the GC/MS system has met tuning criteria and has been calibrated (or has met continuing calibration acceptance criteria), field samples are analyzed after the addition of the ISs. When all compounds of interest have eluted from the gas chromatograph, quantitative analysis is performed using retention times and abundances of the primary quantitation ions of ISs and compounds of interest. Note that a secondary ion may be used to perform quantitative analysis only if analytical interference is encountered for the primary quantitation ion. When a sample extract is analyzed that has a compound of interest with a concentration $ 20% above the upper range of the calibration curve, the extract must be diluted and reanalyzed. A level of dilution that will keep the compounds of interest within the upper half of the calibration range should be used to ensure that no compound has saturated ions. Since the results of the original analysis are used to estimate the dilution factor required, the level of dilution can be difficult to gauge if the shape of the peak indicates that chromatographic saturation has occurred in addition to mass spectrometric detector saturation. A compound with chromatographic as well as mass spectrometric detector saturation may require sequential dilutions. The sample is diluted with hexane in volumetric glassware, the IS concentration is adjusted and the diluted sample is analyzed.

Quantitative analysis is performed using the mean relative response factor from the most recent initial calibration as follows:

$$\text{Concentration} = \frac{A_x I_s V_t D_f}{A_{is} V_i \overline{RRF}} \quad (4.4\text{-}3)$$

Where:

Concentration = concentration of the compound of interest, : g/std m^3

A_x = area response for the primary ion of the compound of interest

A_{is} = area response for the primary ion of the IS

I_s = amount of IS, : g/mL

$\overline{RRF}$ = mean relative response factor from the most recent initial calibration

V_i = volume of air sampled, std m^3

V_t = volume of final extract, mL

D_f = dilution factor for the extract. If there is no dilution, $D_f = 1$. For a diluted sample, $D_f > 1$.

4.4.6.3 Determination of MDLs

As with SVOC measurement, MDLs for PAHs would be most accurately determined by gaseous spiking of the compounds of interest in the field so that the samples would go through the entire sampling and analytical process that field samples experience. This procedure for determination of MDLs is presently not practical, but the closest approximation in the laboratory involves spiking of cleaned certified sorbent so that the samples experience at least the extraction (and cleanup, if used) and analysis portion of the procedure. The procedures of 40 CFR Part 136 Appendix B are used as a guideline for determination of MDLs. To follow the guidelines of

40 CFR Part 136 Appendix B, the following steps are required:

- Estimate the MDLs. This estimate can usually be performed using the calibration standards: if the lowest calibration standard is at a level of 100 picograms (pg)/:L, the analyst can make some estimate of MDLs from this standard.

- Determine a spiking level for the sorbent matrix. At least seven replicate sorbent samples should be spiked with all of the compounds of interest at a level 2 - 5 times the estimated MDLs. For example, if the estimated MDL is 50 pg/:L, the spiking level for the matrix with a 1-mL final extract volume would be gauged to produce a final concentration of compounds of interest in the range of 100 - 250 pg/:L. Surrogate compounds and ISs are spiked at the same level as they are in field samples.

- Prepare and analyze spiked PUF; calculate MDLs. The calculation of the MDLs is based on the standard deviation of the replicate analyses multiplied by the appropriate value of the Student's t corresponding to a 99% confidence level with n - 1 degrees of freedom. The Student's t values at the 99% confidence level are shown in Table 4.4-7.

Table 4.4-7. Student's t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	t
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

The selection of the spiking level is a critical factor in determining the success of the determination. The calculation is based on the reproducibility of the measurement. If the spiking level is too low, chromatographic peaks will be more difficult to integrate, and the reproducibility of the measurement (and hence the MDLs) will suffer. A typical set of MDLs for the EPA Compendium Method TO-13A[10] PAH analytes is shown in Table 4.4-8.

Table 4.4-8. MDLs for EPA Compendium Method TO-13A[10] Analytes: Extraction from Spiked PUF Using Hexane/Ether, Analysis Using SIM

Analyte	Recovery (%)	Method Detection Limit[1] (ng)
acenaphthene	62.2	0.02
acenaphthylene	27.8	0.13
anthracene	43.3	0.08
benz(a)anthracene	74.4	0.04
benzo(a)pyrene	60.0	0.07
benzo(e)pyrene	93.3	0.04
benzo(g,h,i)perylene	98.9	0.03
benzo(b)fluoranthene	126.7	0.04
benzo(k)fluoranthene	67.8	0.03
chrysene	70.0	0.02
coronene	106.7	0.03
dibenz(a,h)anthracene	111.1	0.03
fluoranthene	64.4	0.03
fluorene	61.1	0.03
indeno(1,2,3-cd)pyrene	104.4	0.03
naphthalene	62.2	0.02
perylene	58.9	0.05
phenanthrene	65.6	0.02
pyrene	64.4	0.03

[1]Corrected for recovery.

4.4.6.4 QA/QC

Before analysis of any field samples, the laboratory must demonstrate, by analysis of a LRB, that interferences from the analytical system, glassware and reagents are under control. For each batch of field samples (up to 20 samples) an LRB and LCS must be analyzed and must meet

acceptance criteria. A field blank should be analyzed at a frequency dependent upon the sampling frequency. For a 6-day sampling frequency, one field blank per quarter is sufficient.

Tuning criteria must be met before the initial 5-point calibration is performed; the initial calibration must meet acceptance criteria.

For each day of analysis, tuning criteria must be met and the calibration check sample must be evaluated to verify the stability of the calibration curve and optimal performance of the chromatograph. IS signal areas must meet project specifications, and surrogate compound recoveries should be within a 60 - 120% recovery window. If significant changes are made to the analytical system (i.e., chromatographic column changed, ion source cleaned, quadrupoles cleaned, etc.), the IC must be repeated.

4.5 OVERVIEW OF EPA COMPENDIUM METHOD TO-9A

Sampling of ancient human tissue shows much lower levels of polychlorinated dibenzo-*p*-dioxins and -furans (PCDDs/PCDFs) than are found today[21]. Studies of sediment cores in lakes near industrial centers of the United States have shown that dioxin and furan levels were quite low until about 1920[22-24]. Concentrations of these compounds increased beginning in the 1920s until about 1970, when concentrations began to decline. These trends have been shown to correspond to trends in chlorophenol production[22]. The introduction of dioxin-like compounds into the environment can thus be related to anthropogenic activity. PCDDs and PCDFs are not commercial chemical products but are trace-level unintentional by-products of most forms of combustion and several industrial chemical processes.

PCDDs/PCDFs are dispersed through the environment by atmospheric transport and are found in the environment as complex mixtures of all isomers.[23,24] The isomer profiles of PCDDs/PCDFs found in ambient air are similar to those found in combustion sources. For PCDDs/PCDFs related to specific chemical products and by-products, only a few specific and characteristic isomers are detected. The possible numbers of positional isomers for each member of the PCDD/PCDF chemical family (congeners) are shown in Table 4.5-1.

Table 4.5-1. Possible Number of Positional Isomers at Each Chlorine Level

Chlorine Substitution (Number)	Number of Possible Compounds	
	PCDDs	PCDFs
mono (1)	2	4
di (2)	10	16
tri (3)	14	28
tetra (4)	22	38
penta (5)	14	28
hexa (6)	10	16
hepta (7)	2	4
octa (8)	1	1

The 2,3,7,8-substituted PCDDs/PCDFs are considered to be the most toxic isomers, although they account for only a small percentage of the total concentrations found in stack gas emissions from combustion sources and in ambient air. The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), the most toxic of the PCDDs/PCDFs, is usually found as a very minor component in stack gas emissions and is seldom found in ambient air samples. All of the 2,3,7,8-substituted PCDDs/PCDFs are retained in tissue of life forms such as humans, fish, and wildlife, and the non-2,3,7,8-substituted PCDDs/PCDFs are rapidly metabolized and/or excreted.

Because the PCDDs/PCDFs can be formed by thermal reactions, there has been an increasing interest in ambient air monitoring, especially in the vicinity of combustion and incineration processes such as municipal waste combustors and resource recovery facilities. EPA Compendium Method TO-9A[25] (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-9arr.pdf) can be used for NATTS monitoring, if required, to accurately determine the presence or absence of pg/m^3 or sub-pg/m^3 levels of these compounds in ambient air. The sampling methodology uses a high volume air sampler equipped with a quartz fiber filter and PUF adsorbent for sampling 325 - 400 m^3 of ambient air in a 24-hour sampling period. The analytical procedures used for the field samples are based on HRGC coupled with HRMS. EPA Compendium Method TO-9A[25] provides accurate quantitative data for tetra- through octa-PCDDs/PCDFs, with total concentrations for each isomeric series as well as accurate specific compound concentrations for a limited number of compounds. Specificity is achieved for quantitative determination of the seventeen 2,3,7,8-substituted PCDDs/PCDFs, with MDLs in the range of 0.01 to 0.2 pg/m^3 in ambient air. Concentrations as low as 0.2 pg/m^3 can be accurately quantified. The method does not separately quantify gaseous PCDDs/PCDFs and particulate-associated PCDDs/PCDFs because some of the compounds volatilize from the filter and are collected by the PUF adsorbent. PCDDs and PCDFs may be distributed between the gaseous and particle-adsorbed phases in ambient air, so the filter and PUF are combined for extraction in EPA Compendium Method TO-9A.[25]

Attention has been focused on the determination of PCDDs/PCDFs in ambient air only in recent years. The sample preparation and analysis is time-consuming, complex, difficult and expensive because of the following factors:

- Isotopically labeled standards used in the analysis must incorporate the ^{37}Cl atom as well as ^{13}C, making the standards very expensive to produce and hence to purchase;

- The sample preparation process requires the application of a number of labor-intensive sample cleanup steps to avoid interferences with the analysis, as well as special precautions taken for working with the materials. The 2,3,7,8-TCDD and other 2,3,7,8-substituted isomers are toxic and can pose health hazards if not handled properly. Each of the compounds must be treated as a health hazard, and laboratory staff exposure to these compounds must be minimized. The laboratory staff working with these compounds must follow a strict safety program with an isolated work area, waste handling and disposal procedures, decontamination procedures, and regular wipe testing of the laboratory facilities;

- Because of the high toxicity of specific PCDDs/PCDFs, HRMS must be used to provide the highest possible sensitivity as well as the highest possible level of confidence in the identification of the compound. The instrumentation is complex and expensive, and the computer programs required to reduce the data are also complex and expensive. The analysis must be performed for very low concentrations (pg/m^3 and less), and MDLs must be in the range of 0.01 to 0.2 pg/m^3 to obtain meaningful results for ambient air monitoring purposes.

Quartz fiber filters, PUF plugs and glass adsorbent cartridges are precleaned with appropriate solvents and dried in a clean atmosphere. The PUF is spiked with a known amount of isotopically labeled dioxin standard prior to field deployment. The cartridges and filters are shipped to the field in cleaned, labeled shipping containers. The high volume sampler is put into operation, usually for 24 hours, to sample 325 - 400 m^3 of ambient air. The volume of air sampled is recorded on the COC form shipped to the laboratory with the corresponding filter and PUF. The filter and PUF are combined for sample extraction, the extracts are cleaned up and the sample extracts are subjected to HRGC/HRMS SIM analysis to determine the sampler efficiency, extraction efficiency and the concentrations or the MDLs achieved for the PCDDs/PCDFs. The analytical procedures can be performed to determine only 2,3,7,8-TCDD as the most toxic compound, or the analysis can be performed to determine all possible chlorinated congeners. The analytical results and the volume of air sampled are used to calculate the concentrations of the respective tetra- through octa-isomers, the concentrations of the 2,3,7,8-chlorine-substituted isomers or the MDLs. The concentrations and/or MDLs are reported in pg/m^3.

4.5.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities

Sample collection for quantitative determination of PCDDs/PCDFs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a cartridge containing a PUF plug for the duration of a 24-hour collection period.

4.5.2 Sampling Procedure and Issues Associated with EPA Compendium Method TO-9A[25]

The equipment listed below is required for the collection of samples for the analysis of PCDD/PCDFs.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate of approximately 8 scfm through the filter/PUF plug to obtain a total sample volume greater than 325 scm across a 24-hour duration.

- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the sampler flow path and characterize the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates or a variable orifice device.

- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.

- PUF plugs. The PUF plug is constructed of the polyether type of PUF with a density of 0.022 g/cm^3. The PUF plug is 3-in. thick and has an outside diameter of approximately 2 3/8 in. or approximately 1/8-in. larger in diameter than the opening in the cartridge into which the PUF plug slides.

- Glass sample cartridge. The cartridge used to contain/secure the PUF plug during sample collection is comprised of a thick-walled glass tube outfitted with a stainless steel screen at the outlet end. The cartridge is sized to accomplish a leak-tight fit in the high volume sampler so that all sample air is channeled through the PUF plug.

- Preparation of PUF. The PUF used in sampling is a cylindrical plug 6.0-centimeters (cm) in diameter cut from a 3-in. sheet of PUF. Precleaned PUF can be obtained from commercial sources, but at least one PUF plug from a batch should be extracted and analyzed according to EPA Compendium Method TO-9A procedures to demonstrate that no contamination of the PUF media has occurred. For an initial cleanup, a number of the PUF plugs are placed in a Soxhlet extractor and extracted with acetone for 16 hours at approximately 4 cycles per hour. PUF sampling cartridges may be reused. When the cartridges are reused, diethyl ether/hexane (5 - 10% volume/volume) is used as the cleanup extraction solvent. At least one PUF plug from each batch (either commercially cleaned or laboratory cleaned) should be extracted and analyzed according to the preparation and analytical procedures of EPA Compendium Method TO-9A.[25] A level of 2 - 20 pg for tetra-, penta- and hexachlorodioxins and 40 - 150 pg for hepta- and octachlorodioxins (similar to the levels detected in the method blank) is acceptable. If levels above these criteria are observed, the entire batch of PUF must be recleaned. If the cleaning process is repeated and the PUF still cannot meet the cleanliness criteria, the batch of PUF (and possibly the sheet from which the plugs were cut) must be discarded. Cartridges are considered clean for up to 30 days from date of certification when stored in their sealed containers. Prior to deployment with the sampling system, the PUF cartridges are spiked with isotopically labeled surrogate compounds, as shown in Table 4.5-2. The surrogate compound solution is added to each PUF sampling cartridge, in the center of the bed of the PUF cartridge, using a microsyringe.

4.5.2.1 Sampling Procedure

The sampler should be located in an unobstructed area at least 2 m from any obstacle to airflow with the inlet positioned in the breathing zone, 4 - 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head. When a new sampler is set up or when the sampler is used at a different location, all areas of the sampling apparatus that contact the sample need to be cleaned using

Table 4.5-2. Native and Isotopically Labeled Standards

Native Compounds	Internal Standards
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-2,3,7,8-tetrachlorodibenzo-*p*-dioxin
2,3,7,8-tetrachlorodibenzofuran	$^{13}C_{12}$-1,2,3,7,8-pentachloro-*p*-dibenzodioxin
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-1,2,3,6,7,8-hexachloro-*p*-dibenzodioxin
1,2,3,7,8-pentachlorodibenzofuran	$^{13}C_{12}$-1,2,3,4,6,7,8-heptachloro-*p*-dibenzodioxin
2,3,4,7,8-pentachlorodibenzofuran	$^{13}C_{12}$-octachlorodibenzo-*p*-dioxin
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-2,3,7,8-tetrachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-1,2,3,7,8-pentachlorodibenzofuran
1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-1,2,3,4,7,8-hexachlorodibenzofuran
1,2,3,4,7,8-hexachlorodibenzofuran	$^{13}C_{12}$-1,2,3,4,6,7,8-heptachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzofuran	**Surrogate Standards**
1,2,3,7,8,9-hexachlorodibenzofuran	$^{13}C_{12}$-2,3,4,7,8-pentachlorodibenzofuran
2,3,4,6,7,8-hexachlorodibenzo-*p*-dioxin	$^{13}C_{12}$-1,2,3,4,7,8-hexachloro-*p*-dibenzodioxin
1,2,3,4,6,7,8-heptachloro-*p*-dibenzodioxin	$^{13}C_{12}$-1,2,3,6,7,8-hexachlorodibenzofuran
1,2,3,4,6,7,8-heptachlorodibenzofuran	$^{13}C_{12}$-1,2,3,6,7,8,9-heptachloro-*p*-dibenzodioxin
1,2,3,4,7,8,9-heptachlorodibenzofuran	**Field Standards**
octachlorodibenzo-*p*-dioxin	$^{37}Cl_4$-2,3,7,8-tetrachlorodibenzo-*p*-dioxin
octachlorodibenzofuran	$^{13}C_{12}$-1,2,3,7,8,9-hexachloro-*p*-dibenzodioxin
Recovery Standard	
$^{13}C_{12}$-1,2,3,4-tetrachlorodibenzo-*p*-dioxin	

triple rinses of reagent-grade hexane contained in Teflon wash bottles. All cleaning and washing should be done in a controlled environment to minimize contamination. Solvent should be allowed to evaporate before the PUF sampling module is loaded into the sampler.

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-9A.[25] The individual orifice plates are placed in the sampling flow stream, and the

differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of the sampler.

Sample Collection

The prepared PUF cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually, and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the PUF plug. The PUF cartridge is then removed from the high volume sampler and transported to the laboratory.

4.5.3 Analytical Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field samples. The most important member of the compound class measured for the NATTS Program is 2,3,7,8-TCDD (CAS No. 1746-01-6).

4.5.3.1 Equipment, Materials, Reagents and Standards

The analysis is performed using HRGC/HRMS. The GC must be programmable and designed for use of capillary chromatographic columns. The injection technique selected and the injection volume must be used consistently throughout the series of analyses. The capillary column must be fitted directly into the ion source of the mass spectrometer. Since graphite ferrules can adsorb PCDDs/PCDFs, Vespel® or equivalent inert ferrules must be used. The MS is operated in the electron ionization mode, using the isotope dilution SIM procedures specified in EPA

Compendium Method TO-9A,[25] with a total cycle time of 1 second or less. The static resolving power of the mass spectrometer (MS) must be maintained at 10,000 or greater (10% valley definition). The data system must control the MS, data acquisition and data processing, with the capability of controlling and switching to different sets of ions according to EPA Compendium Method TO-9A[25] protocol.

Capillary chromatography columns are needed to perform the analysis, either the columns specified in EPA Compendium Method TO-9A[25] or alternatives that have been demonstrated to meet the method performance requirements.

Standard laboratory equipment such as hoods, rotary evaporator, balances, etc., is specified in EPA Compendium Method TO-9A.[25]

Standard laboratory reagents and high purity solvents required for performance of the method are described in EPA Compendium Method TO-9A.[25] The native and isotopically labeled dioxin/furan standards required for performance of EPA Compendium Method TO-9A[25] are shown in Table 4.5-2. The compounds listed in Table 4.5-2 are used in the preparation of calibration standards, sample fortification solutions, recovery standard spiking solution, sampler field fortification solution, and matrix/method spike solutions.

An additional set of dioxin/furan standards is used to define the first and last compound at each chlorination level to elute from the chromatographic column. The exact standard used for this purpose depends upon the chromatographic columns selected.

4.5.3.2 Sample Preparation

Samples collected in the field should be shipped and stored at a temperature <4°C until receipt at the analytical laboratory. At the laboratory, the samples should be refrigerated at #4°C. Extraction of the samples must be performed within seven days of sampling, and the extracts must be analyzed within 40 days after extraction.

Glassware Cleanup

For preparation of dioxin/furan samples, each piece of glassware should go through the cleaning process separately, except for oven baking. Each vessel should be washed three times with hot tap water, twice with acetone and twice with hexane prior to being baked for 16 hours at 450°C in a forced air oven that is vented to the outside. The PTFE stopcocks should be cleaned as described above, except for oven baking. All glassware should be rinsed with acetone and hexane immediately before use.

Acid/Base Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The PUF plug and the quartz fiber filter are removed from the glass sample cartridge and placed in a Soxhlet extractor. An aliquot of the isotopically labeled sample fortification solution (a solution of the ISs, as shown in Table 4.5-2) is added to the sample prior to extraction. EPA Compendium Method TO-9A[25] originally specified benzene as the extracting solvent, but because of the health hazards associated with the use of benzene, toluene should be used as the extraction solvent. After a 16-hour extraction and solvent exchange into a final volume of 25 mL of hexane, acid-base cleanup is performed using 2N potassium hydroxide for a maximum of four washes until no color is visible in the aqueous layer, a partition against sodium chloride solution, and acid wash using concentrated sulfuric acid, until no color is visible in the aqueous layer, up to a maximum of four washes. After partitioning against sodium chloride solution, dry the extract and concentrate using a Kuderna-Danish concentrator and a steam bath to a final volume of 1 - 2 mL. The extract is ready for alumina column cleanup at this point, but it can be sealed and stored in the dark, if necessary. Method instructions call for acid/base cleanup with repeated acid/base washes (up to a maximum of four) to ensure removal of color from the aqueous layer. If color remains after the acid/base cleanup (probably yellow or brown), a silica column cleanup is required before the alumina cleanup.

Silica Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

If silica column cleanup is required, silica gel columns are prepared according to the instructions of EPA Compendium Method TO-9A.[25] The prepared columns are stored in an oven set at 220°C until ready for use (or at least overnight). Silica columns should be removed from the oven when needed and placed in a desiccator until they have equilibrated to room temperature, then used immediately. The silica gel column is eluted with hexane, and the eluate is subjected to alumina column cleanup.

Alumina Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The alumina column is prepared according to EPA Compendium Method TO-9A[25] instructions and prewashed with methylene chloride. Methylene chloride is forced from the alumina column with a stream of dry nitrogen, and prepared columns are stored in an oven set at 225°C until they are ready for use (at least overnight). Columns should be removed from the oven only when needed, placed in a desiccator over anhydrous calcium sulfate until they have equilibrated to room temperature, and used immediately. The hexane extract is placed into the column and eluted according to the instructions of EPA Compendium Method TO-9A.[25] After alumina column cleanup, the extract is ready for carbon column cleanup.

Carbon Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The carbon column is prepared using silica gel and carbon according to the instructions of EPA Compendium Method TO-9A,[25] eluted according to the Method, and all elution solvents are archived. When the extract has been eluted with toluene, add tetradecane and concentrate to a final volume of 5 mL using a stream of dry nitrogen and a water bath maintained at 60°C. The recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, is added after the carbon column cleanup is complete; the extract may then be stored in the dark at room temperature. Immediately prior to analysis, the extract is concentrated to 30 :L using a stream of nitrogen at room temperature. Immediately prior to analysis, the sample is diluted to a final volume of 100 :L with toluene.

4.5.3.3 Interferences and Contamination

As in all chromatographic analytical methods, any compound with a similar mass eluting from the HRGC column within ±2 seconds of a compound of interest is a potential interference. Any compound eluting from the HRGC column in a very high concentration will decrease overall instrument sensitivity in a given retention time window. If the interfering compound has a sufficiently high concentration, the mass assignments in the retention time window may be changed and the compound of interest may not be observed at all. Compounds that are chemically similar and hence extracted with PCDDs/PCDFs are also common interferences. These interfering compounds include polychlorinated biphenyls (PCBs), methoxybiphenyls, polychlorinated diphenyl ethers, polychlorinated naphthalenes, the pesticides *p,p*'-dichlorodiphenyldichloroethylene (DDE) and *p,p*'-dichlorodiphenyltrichloroethane (DDT), etc. Cleanup procedures in EPA Compendium Method TO-9A[25] are carefully designed to remove most of these types of substances, but the cleanup procedures are not guaranteed to be 100% efficient in all situations. The chromatographic resolution of the capillary column and the mass resolution of the mass spectrometer are also helpful in removing interferences from the compounds of interest. Polychlorinated diphenyl ethers are extremely difficult to resolve from PCDFs because of their chemical similarity, because they elute in the same retention time windows as PCDFs, and because of the similarity of their mass spectrometric fragmentation pattern.

Because the analysis is performed at such low concentration levels, minimization of potential interferences is critical. High purity reagents and solvents must be used, and all glassware and equipment must be scrupulously cleaned. All materials used in the laboratory procedures must be monitored and analyzed frequently to ensure that they are not contaminated.

4.5.3.4 Preparation of the Analytical System

The HRGC/HRMS system is operated in the electron ionization (EI) mode using SIM detection. Before analysis of a set of samples is initiated, the instrument must achieve a static mass resolution of 10,000 (10% valley, tuning at mass 292.9825 of perfluorokerosene (PFK)), with corrective action implemented if the instrument does not meet the requirements. Instrument mass resolving power is verified according to the procedures of EPA Compendium Method

TO-9A.[25] To avoid problems with mass drifts over the long chromatographic elution time required for the dioxin/furan analysis, a lock mass ion for the reference compound (PFK) is used to tune the MS. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each mass window can be used to monitor and correct any mass drifts of the MS. The level of PFK in the ion source should be kept at the lowest level possible to allow effective monitoring of changes in sensitivity. If the level of PFK in the instrument is too high, high background signals will be observed and the ion source will become contaminated. Contamination decreases instrument sensitivity and requires downtime for instrument maintenance. Table 10 of EPA Compendium Method TO-9A[25] shows the five mass windows used to monitor the dioxins/furans (tetrachloro- through octachloro-, one window for each level of chlorination), the accurate masses monitored to four decimal places (different accurate masses based on the combination of masses 35/37 for chlorine and masses 12/13 for carbon), a PFK lock mass, and a PFK QC mass. Accurate masses for the diphenyl ether isomers are also included at the appropriate retention times. The total time for each SIM cycle should be one second or less for data acquisition, including the sum of the mass ion dwell times and electrostatic analyzer voltage reset times (i.e., 1 second start-to-start).

Two HRGC columns have been used successfully in the EPA Compendium Method TO-9A[25] analysis since 1984:

- DB-5 (60 m). Provides an efficient analysis for total concentrations of PCDDs/PCDFs, specific isomers (total tetra-, penta-, hexa-CDDs/CDFs, four heptachlorodibenzofuran isomers, two heptachlorodibenzodioxin isomers, octachlorodibenzodioxin, and octachlorodibenzofuran) and determination of MDL.

- SP-2331 (60 m). Provides demonstrated and confirmed resolution of 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs/CDFs.

Other capillary columns may be used if the performance satisfies the specifications for resolution of PCDDs/PCDFs. After the capillary column has been selected and the HRMS parameters are optimized, an aliquot of the column performance solution should be analyzed to determine and confirm SIM parameters, retention time windows, and chromatographic resolution

of the compounds. The chromatographic peak separation between 2,3,7,8-TCDD and the coeluting isomers must resolved with a valley of 25% or more. The retention order of the compounds will be determined by the chromatographic column used.

4.5.3.5 Determination of MDLs

The MDL is defined as the amount of an analyte required to produce a signal with a peak area at least 2.5 times the area of a background signal level measured at the retention time of interest. MDLs are calculated for total PCDDs/PCDFs and for each 2,3,7,8-substituted congener. Ambient levels of total PCDDs/PCDFs are usually observed in the range of 0.3 - 2.9 pg/m^3. To generate meaningful data for ambient air, the MDL for tetra-, penta-, and hexa-CDDs/CDFs should be in the range of 0.02 - 0.15 pg/m^3. Trace levels of heptachlorodibenzodioxins and octachlorodibenzodioxin (0.05 - 0.25 pg/m^3) are usually detected in the method blank.

The MDL is calculated according to Equation 4.5-1.

$$MDL = (2.5 \times A_x \times Q_{is}) / (A_{is} \times V_{std} \times mRRF) \quad (4.5\text{-}1)$$

Where:

MDL = concentration of unlabeled PCDD/PCDF, pg/m^3

A_x = sum of integrated ion abundances of the quantitation ions for the unlabeled PCDDs/PCDFs which do not meet the ID criteria of 2.5 × area of noise level at the analyte retention time

A_{is} = sum of the integrated ion abundances of the quantitation ions for the $^{13}C_{12}$-labeled IS

Q_{is} = quantity of the $^{13}C_{12}$-labeled IS spiked into the sample prior to extraction, pg

V_{std} = standard volume of ambient air sampled, std m^3

mRRF = mean relative response factor for the unlabeled PCDD/PCDF.

If response signals for one or both quantitation ions at the retention time of the 2,3,7,8-substituted isomer (or at the retention time of non-2,3,7,8-substituted isomers) are absent, the instrument noise level is measured at the expected retention time of the analyte and multiplied by 2.5, inserted into Equation 4.5-1, and calculated and reported as not detected (ND) at the specific MDL.

Response signals at the same retention time as the 2,3,7,8-substituted isomers or the other isomers that have a signal-to-noise ratio in excess of 2.5:1 but do not satisfy the identification criteria are calculated and reported as ND at the elevated MDL and discussed in the narrative that accompanies the analytical results.

4.5.3.6 IC for Analysis of Field Samples

After the HRGC/HRMS SIM operating conditions have been optimized, an initial five-point calibration is performed using calibration solutions with the concentrations shown in Table 4.5-3.

Quantification relationships between labeled and unlabeled standards are shown in Tables 15, 16, and 17 of EPA Compendium Method TO-9A.[25] After the calibration solutions have been analyzed, the relative response factors for each unlabeled compound relative to its corresponding

$^{13}C_{12}$-labeled internal standard are calculated according to Equation 4.5-2.

$$RRF(I) = (A_x \times Q_{is}) / (Q_x \times A_{is}) \qquad (4.5\text{-}2)$$

Table 4.5-3. Composition/Concentrations of the IC Solutions

Calibration Solution	Concentrations (pg/:L)				
	1	2	3	4	5
Unlabeled Analytes					
2,3,7,8-tetrachlorodibenzodioxin	0.5	1.0	5.0	50	100
2,3,7,8-tetrachlorodibenzofuran	0.5	1.0	5.0	50	100
1,2,3,7,8-pentachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,7,8-pentachlorodibenzofuran	2.5	5.0	25	250	500
2,3,4,7,8-pentachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,4,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,6,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,7,8,9-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,4,7,8-hexachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,6,7,8-hexachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,7,8,9-hexachlorodibenzofuran	2.5	5.0	25	250	500
2,3,4,6,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,4,6,7,8-heptachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,4,6,7,8-heptachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,4,7,8,9-heptachlorodibenzofuran	2.5	5.0	25	250	500
octachlorodibenzodioxin	5.0	10	50	500	1000
octachlorodibenzofuran	5.0	10	50	500	1000
Internal Standards					
$^{13}C_{12}$-2,3,7,8-tetrachlorodibenzodioxin	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-pentachlorodibenzodioxin	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-hexachlorodibenzodioxin	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-heptachlorodibenzodioxin	100	100	100	100	100
$^{13}C_{12}$-octachlorodibenzodioxin	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-tetrachlorodibenzofuran	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-pentachlorodibenzofuran	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-hexachlorodibenzofuran	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-heptachlorodibenzofuran	100	100	100	100	100

(Continued)

Table 4.5-3. (Continued)

Calibration Solution	Concentrations (pg/:L)				
	1	2	3	4	5
Internal Standards (Continued)					
$^{13}C_{12}$-2,3,4,7,8-pentachlorodibenzofuran	60	80	100	120	140
$^{13}C_{12}$-1,2,3,4,7,8-hexachlorodibenzodioxin	60	80	100	120	140
$^{13}C_{12}$-1,2,3,6,7,8-hexachlorodibenzofuran	60	80	100	120	140
$^{13}C_{12}$-1,2,3,6,7,8,9-heptachlorodibenzodioxin	60	81	100	120	140
Field Standards					
$^{37}Cl_4$-2,3,7,8-tetrachlorodibenzodioxin	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-hexachlorodibenzodioxin	100	100	100	100	100
Recovery Standard					
$^{13}C_{12}$-1,2,3,4-tetrachlorodibenzodioxin	50	50	50	50	50

Where:

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the $^{13}C_{12}$-labeled internal standards.

RRFs for $^{13}C_{12}$-labeled PCDD/PCDF ISs relative to the $^{37}Cl_4$-2,3,7,8-tetrachloro-dibenzodioxin recovery standard are calculated according to Equation 4.5-3.

$$RRF(II) = (A_{is} \times Q_{rs}) / (Q_{is} \times A_{rs}) \quad (4.5\text{-}3)$$

Where:

A_{rs} = integrated ion abundance for the quantitation ion of the $^{37}Cl_4$-2,3,7,8-TCDD recovery standard

Q_{is} = quantity of the $^{13}C_{12}$-labeled IS injected, pg

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected, pg

Q_{rs} = quantity of the $^{37}Cl_4$-2,3,7,8-TCDD injected, pg.

The RRFs are dimensionless quantities. The average relative response factors for the five concentration levels of the calibration standards are calculated by dividing the mean of the five RRFs by five.

Acceptance Criteria for the Initial Calibration

For an acceptable calibration, the analytical data must satisfy the acceptance criteria contained in Tables 19 and 20 of EPA Compendium Method TO-9A.[25] The isotope ratios must be within the acceptable range, and the percent RSD for the response factors should be less than the values shown in Table 21 of EPA Compendium Method TO-9A.[25] The signal-to-noise ratio for the $^{13}C_{12}$-labeled standards must be 10:1 or more; the signal-to-noise ratio for the unlabeled standards must be 5:1 or more.

Continuing Calibration

At the beginning of each day a continuing calibration analysis should be performed to check and confirm the continuing stability of the calibration. An aliquot of one of the calibration standards (a mid-range standard) is used to perform the continuing calibration check. The continuing calibration analysis must meet the criteria for acceptability of the isotope ratios and the signal-to-noise ratios for the initial calibration. The continuing stability of the calibration should also be verified at the end of the day. The percent difference for the continuing calibration check is calculated using Equation 4.5-4.

$$\%\text{Difference} = [(RRF_{cc} - \text{mRRF})/\text{mRRF}] \times 100 \qquad (4.5\text{-}4)$$

Where:

RRF_{cc} = RRF for a specific analyte in the continuing calibration standard

mRRF = mean response factor from the IC curve.

4.5.3.7 Analytical Procedure

An aliquot of the cleaned up sample extract is analyzed with the HRGC/HRMS system using the optimized instrument parameters and the exact masses that have been established for the dioxin/furan analysis. The following criteria are used for the identification of PCDDs/PCDFs in samples:

- The integrated ion abundance for M/(M+2) or (M+2)/(M+4) shall be within ±15% of the theoretical value. Acceptable control limits for the ion abundance ratios are shown in Tables 19 and 20 of EPA Compendium Method TO-9A.[25]
- The ions monitored for a given analyte must maximize within 2 seconds of each other.
- The retention time for the 2,3,7,8-substituted analytes must be within 3 seconds of the corresponding $^{13}C_{12}$-labeled IS or surrogate standard.
- The ID of 2,3,7,8-substituted isomers that do not have corresponding $^{13}C_{12}$-labeled standards must be done by comparison to the analysis on the same chromatographic column of a standard that contains the specific congeners. The RRT of the analyte must be within 0.005 RRT units of the comparable RRTs of the analyte and the nearest eluting internal standard found in a separate analysis.
- The signal-to-noise ratio for the monitored ions must be >2.5.
- The analysis shall show that polychlorinated diphenyl ethers are not present. Any polychlorinated diphenyl ethers that elute within ±2 seconds of PCDF peaks indicate a positive interference, especially if the intensity of the polychlorinated diphenyl ether peak is 10% or more of the PCDF peak.

Peak areas for the ions of $^{13}C_{12}$-labeled PCDDs/PCDFs, $^{37}Cl_4$-2,3,7,8-TCDD, unlabeled PCDDs/PCDFs, and the respective RRFs are used for quantitative analysis:

- $^{37}Cl_4$-2,3,7,8-TCDD is spiked into the extract prior to final concentration. Calculated relative response factors are used to determine the sample extraction efficiencies (% recoveries) for the nine $^{13}C_{12}$-labeled ISs, which were spiked into the sample prior to extraction .

- The $^{13}C_{12}$-labeled PCDD/PCDF ISs and response factors are used for quantitative calculation of unlabeled PCDDs/PCDFs and for determination of MDLs. (However, $^{13}C_{12}$-octachlorodibenzodioxin is used for octachlorodibenzofuran). Each $^{13}C_{12}$-labeled IS is used to quantify all of the PCDDs/PCDFs in its isomeric group.

- The $^{37}Cl_4$-2,3,7,8-TCDD spiked onto the PUF prior to sampling is used to determine the collection efficiency for the sampling period.

4.5.3.8 Calculations

Extraction Efficiency.

The extraction efficiencies (% recovery) of the nine $^{13}C_{12}$-labeled PCDDs/PCDFs measured in the extract are calculated using the Equation 4.5-5.

$$\%R_{is} = [A_{is} \times Q_{rs} \times 100]/[Q_{is} \times A_{rs} \times RRF(II)] \quad (4.5\text{-}5)$$

Where:

$\%R_{is}$ = percent recovery (extraction efficiency)

A_{is} = sum of the integrated ion abundances of the quantitation ions for the $^{13}C_{12}$-labeled IS

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the $^{37}Cl_4$- or the $^{13}C_{12}$-labeled recovery standard

Q_{is} = quantity of the $^{13}C_{12}$-labeled IS added to the sample before extraction, pg

Q_{rs} = quantity of the $^{37}Cl_4$- or $^{13}C_{12}$-labeled recovery standard added to the sample extract before analysis, pg

RRF(II) = calculated mean RRF for the labeled IS relative to the appropriate labeled recovery standard (Equation 4.5-3).

Analyte Concentration

The concentration of each 2,3,7,8-substituted PCDD/PCDF that has met ID criteria is calculated using Equation 4.5-6.

$$C_x = (A_x \times Q_{is}) / [A_{is} \times V_{std} \times RRF(I)] \quad (4.5\text{-}6)$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congener(s), pg/m^3

A_x = sum of the integrated ion abundances of the quantitation ions for the unlabeled PCDDs/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the respective $^{13}C_{12}$-labeled IS

Q_{is} = quantity of the $^{13}C_{12}$-labeled IS added to the sample before extraction, pg

V_{std} = standard volume of air sampled, std m^3

RRF(I) = calculated mean RRF for an unlabeled 2,3,7,8-substituted PCDD/PCDF (Equation 4.5-2).

4.5.4 Quality Assurance/Quality Control

Certified analytical standards, both native compounds and isotopically labeled standards, are available through Cambridge Isotope Laboratories and from a number of other distributors. IC and continuing calibration analyses must meet EPA Compendium Method TO-9A[25] acceptance criteria. Compounds must meet EPA Compendium Method TO-9A[25] ID criteria. All field samples, method blanks, field blanks, and LCSs must be spiked with $^{13}C_{12}$-labeled ISs prior to extraction. Sample preparation , analysis, and data evaluation are performed on a set of 12 samples consisting of 9 field samples, field blank, method blank, fortified method blank, or an

LCS. The $^{13}C_{12}$-1,2,3,4-TCDD standard is spiked onto the PUF plugs prior to shipping them to the field for sampling in order to determine and document the sampling efficiency. Quality assurance/quality control requirements for the data are summarized in Table 4.5-4.

Table 4.5-4. QA/QC Requirements for EPA Compendium Method TO-9A Data

Criterion	Requirement
Satisfy ID criteria	Integrated ion abundance ratio within ±15% of theoretical ions monitored for a given analyte maximize within 2 seconds of each other Retention time for 2,3,7,8-substituted analytes must be within 3 seconds of the corresponding $^{13}C_{12}$-labeled IS or surrogate 2,3,7,8-isomers without $^{13}C_{12}$-standards meet method ID criteria Signal-to-noise ratio for monitored ions >2.5 Absence of polychlorinated diphenyl ethers
Recoveries for $^{13}C_{12}$-labeled tetra-, penta-, hexa-CDDs/CDFs	50 - 120%
Recoveries for $^{13}C_{12}$-labeled heptachlorodibenzodioxin and octachlorodibenzodioxin	40 - 120%
Accuracy achieved for PCDDs/PCDFs in method spike at 0.25 - 2.0 pg/m^3	70 - 130%
Precision achieved for duplicate method spikes or quality assurance samples	±30%
Recovery of PUF prespike	50 - 120%
Method blank contamination	Free of contamination that would interfere with field sample results
MDL range for method blank and field blank (individual isomers)	0.02 - 0.25 pg/m^3

4.6 AEROSOL BLACK CARBON MEASUREMENT PROCEDURE

Carbon is one of the most abundant constituents of ambient particulate matter. Carbon is typically represented as organic carbon (OC), which is volatile, and elemental carbon (EC), which is inert, and carbonate carbon wich is the inorganic carbon fraction found in minerals. Optical

absorption measurement techniques are used to provide a measure of the inert portion of carbon usually referred to as black carbon (BC). There is much debate in the scientific community regarding chemical and physical definitions of OC, EC and BC. As this time, the differentiation of OC from EC and BC is dependent on the specific measurement analysis technique and operational procedures used. BC and EC are often used synonymously to refer to the graphitic-like, inert, light absorbing carbon without distinction or clarification regarding the operational definitions. Since there are no reference standards for assessing the measurement of 'true' OC, EC and BC or a standardized method for distinguishing between these species, differing results are obtained depending on the collection and analysis method used. In order to avoid confusion and for the purposes of this discussion, BC will be used to refer to the light absorbing carbon measured by optical absorption with the Aethalometer™. The chemical and physical characteristics of BC are assumed to be the same as EC.

BC is insoluble in polar and nonpolar solvents, and is stable in air or oxygen at temperatures up to approximately 350 - 400°C. BC displays the Raman spectral shifts characteristic of a graphitic ring structure, but in a disordered microcrystalline form. The reason that ambient particulate material appears black when collected on a filter is due to the presence of light absorbing BC. Particulate BC is ubiquitous in the atmosphere, present at levels ranging from 0.05 - 300 ng/m^3 in remote areas[26-31] and up to 13.3 : g/m^3 in urban areas.[31] The value of 13.3 : g/m^3 can go up or down depending upon the method and sampling interval. BC is produced only by combustion processes involving carbonaceous material; BC is not generated by any known atmospheric reactions.[26-28] The levels of BC can exceed 30-40 : g/m^3 in areas with a large combustion source influences. BC is predominantly present in submicron particles,[26,32-35] and can have a lifetime in the atmosphere ranging from several days to several weeks, depending upon the meteorology.[31] Ambient measurement data indicate that long-range transport becomes important[26,27,29,31] because of the long lifetime for BC. BC can be regional in nature, especially in remote areas, but local sources are usually dominant.[26,31] BC plays an important role in atmospheric chemistry because of its catalytic properties[26,31,33,36] and affects visibility by light extinction.[31,33,37,38] BC is strongly optically absorbing. Because of its absorption of light, BC is potentially climate-altering.[31,33,38]

4.6.1 Overview of BC Measurement

Aerosol BC is most visually obvious in diesel exhaust, but it is also emitted from all combustion sources together with other species such as toxic and carcinogenic organic compounds. The Aethalometer™ (Berkeley, CA; http://www.mageesci.com) is an instrument that measures the optically absorbing aerosol fraction of particulate matter from the sampled airstream, in near-real-time using a continuous filtration and optical transmission technique. The Aethalometer™ operates at a wavelength of 880 nm (in the near-IR range). At this wavelength, the only aerosol species expected to have a high, optical absorption cross-section is BC. Due to high time resolution, the Aethalometer™ measurements have the ability to show emissions patterns according to the diurnal cycle of sources (e.g., weekday vs. weekend traffic). In more remote locations, the time-resolved data obtained from the Aethalometer™ measurements reflect medium- or long-range transport of emissions from the source area to the receptor (i.e., meteorology). The Aethalometer™ was developed as an effective real-time analyzer for measuring particle light absorption; results are reported as BC concentration in the atmosphere. The Aethalometer™ collects aerosol continuously on a quartz fiber filter tape, and determines the increment of optically absorbing material collected per unit volume of sampled air.

4.6.2 General Description of Measurement Method

The principle of the Aethalometer™ is to measure the attenuation of a beam of light transmitted through a filter while the filter is continuously collecting an aerosol sample. The measurement is made at successive regular intervals of a timebase period. By using a value of the specific attenuation for the particular combination of filter and optical components, the BC content of an aerosol deposit can be determined at each measurement time. The increase in optical attenuation from one period to the next is due to the increment of aerosol BC collected from the airstream during the period. Dividing this increment by the volume of air sampled during that time determines the mean BC concentration in the sampled airstream during the period.

The objectives of the Aethalometer™ hardware and associated software are to:

- collect the aerosol sample with as few losses as possible on a quartz filter material;
- measure the optical attenuation of the collected aerosol deposit as accurately as possible;
- calculate the rate of increase of the BC component of the aerosol deposit and to interpret this rate of increase as a BC concentration in the airstream; and
- display and record the data, and to perform necessary instrument control and diagnostic functions.

The configuration of the Aethalometer™ includes a filtration and analysis chamber with automatically advancing quartz fiber tape, sample aspiration pump, air mass flow meter or controller (a typical flow rate is 5 Lpm), and temperature-stabilized optics and electronics. The instrument is operated by an embedded computer that controls all instrument functions and records data directly onto a 3.5 inch floppy disk; an analog and RS-232 output are available for use with data acquisition systems to allow remote polling of the data.

Measurement of BC for the NATTS requires the application of an Aethalometer™ in the "big spot" configuration (Magee Scientific designation of "-ER" after the model number). The "big spot" configuration provides a larger impaction area on the tape than the standard model. For the NATTS application, BC measurements are made using a Magee Scientific AE-16 nonportable Aethalometer™ with a BGI $PM_{2.5}$ inlet (SCC 1.829). Any Aethalometer™ model can be "big spot" if "-ER" is affixed to the model number. If the AE-21 dual channel unit is used, the UV channel should be turned off to reduce the number of tape advances and lost data. The BGI, Inc. (Waltham, MA; http://www.bgiusa.com) cyclone is designed to exclude particulate matter larger than 2.5 : m in aerodynamic diameter when operated at the prescribed flow rate of 5.0 Lpm.

4.6.3 Interferences

The measurement is insensitive to extractable organic carbon or other aerosol species that substantially contribute to the total aerosol mass, and are not optically absorbing, implying that BC is the only aerosol species that is optically absorbing in the visible spectrum and that a

measurement of visible light absorption may be interpreted directly in terms of a mass of BC. This observation is generally valid for aerosol samples taken from sources and in urban and many remote areas but is not valid when the sample contains a very large amount of mineral dust. Dust has an absorption cross section that is smaller than that of BC by a factor of 100 - 1000. If the amount of mineral dust is 100 - 1000 times greater than the amount of BC, a comparable optical absorption may be produced. This interference cannot be eliminated in the real-time measurements of the Aethalometer™, though it can be determined in a subsequent analysis of the filter sample.

It is also important to protect the BC aerosol inlet from two macroscopic contaminants, rain and insects. The quartz fiber filter will clog and will dramatically change its optical properties if it becomes wet, so it is very important that rain, spray, or any other water be excluded. The use of a trap is highly recommended if there is any possibility of rain or other water entry. It is also necessary to exclude insects from the inlet, since a small mosquito sucked onto the filter can cause an extremely large change in optical transmission and increased signal noise that will certainly invalidate the data collected during that period.

The Aethalometer™ tape advances automatically to avoid overload and saturation of optical absorption due reduced transmission. The tape advances to a clean spot when an optical absorption depth of 0.75 is reached, which corresponds to a surface loading of about 4 $\mu g/cm^2$. During tape advance, the system temporarily halts data collection, advances the tape and reinitializes prior to resuming data collection. The amount of time required to complete the process is a function of collection timebase and tape advance settings. During this period, no data are collected. For a timebase of 5 minutes, 15 minutes will be required and result in lost data for this period. The rate of accumulation of BC on the spot is proportional to both the BC concentration in the airstream and to the airflow rate. To minimize the number of tape advances and amount of data lost in urban areas where the ambient concentrations of BC are expected to be higher, the ER (increased spot size) version of Aethalometer™ is recommended with a timebase no longer than 5 minutes.

4.6.4 Operational Procedure

The following section applies only to the configuration of the single-channel Aethalometer™, Model AE-16-ER. Dual-channel AE-21-ER units are optional; however, it is recommended that the UC channel be turned off in urban areas where BC concentrations are high and frequent tape advances cause more than 25% incomplete hourly data. The Aethalometer™ ER can accurately measure an increment of about 3 ng of BC on its filter. At a flow rate of 5 Lpm and a timebase of 5 min, this corresponds to a resolution corresponding to 0.12 : g/m^3. System specifications are shown in Table 4.6-1.

Table 4.6-1. Aethalometer™ Specifications (Model AE-16-ER) for NATTS

Parameter	Specification
Filtration Medium	Quartz fiber tape, 15-m tape rolls. Sample collection proceeds on an 1.67 cm^2 oval spot until a threshold BC loading density is reached, at which point the tape advances. Each roll of tape accommodates about 1500 spots.
Pumping and Sample Airflow Rate	Includes an internal 1 - 10 Lpm mass flow meter. Vacuum can be provided either by an internally mounted diaphragm pump or an external sampling pump.
Optics and Electronics	Stabilized solid-state light source at 880 nm, 24-bit A/D conversion of photometric signals. Active temperature stabilization of electronics.
Operator Interface	Display panel with keypad, status lights, and 4-line screen.
Computer	Embedded computer runs automatically upon power-up; recovers from power failures. Calculates BC concentrations directly in ng/m^3.
Data acquisition	Automatically stores data to on-board 3.5 inch floppy disk or analog and RS-232 output to data acquistion device.
Electrical Specifications	120 or 240 vAC, 50/60 Hz, 60 watts maximum
Ambient $PM_{2.5}$ Inlet	The inlet used with the Aethalometer™ is a BGI "Photometer" Cyclone (Model SCC 1.829), featuring dry sampling (no oil or grease). This unit has a 2.5-: cut at 5 Lpm. The SCC model also has a very low-pressure drop at design flow rates, and requires a vertical inlet tube. The cyclone is held to this tube by a pair of internal O-rings.

4.6.4.1 Filtration Medium

The Aethalometer™ is operated with web-reinforced, quartz fiber filter tape. This material has a deep mat of optically scattering fibers within which the aerosol particles are collected, with the result of nullifying any effect on optical transmission by light scattering from the particles that have been collected. The measurement is therefore sensitive only to incremental light absorption. The Aethalometer™ must use a deep fibrous type of filter for correct operation. In manufacture, the quartz fiber material is laid down upon a reinforcing web of cellulosic material to provide mechanical strength: the pure quartz material itself is extremely brittle and friable, with little mechanical strength. The material must be handled with some care

and requires the use of the web underlayer to perform automatic tape handling. The cellulosic backing material prohibits the use of this tape for subsequent thermal analysis.

An additional feature of the Aethalometer™ that can be used to avoid overloading and to prolong the life of the tape in an urban environment is the "tape saver" feature. The tape saver controls a flow bypass valve that can divert the flow of particulate-laden sample air away from the filter spot for a controllable fraction of each timebase period. This feature reduces the amount of sample accumulation in high aerosol concentrations by a known fraction that is accounted for in the BC calculation algorithm. Use of the tape saver prolongs the life of each filter tape spot and thus reduces the consumption of tape and the interruptions to data collection due to tape advance and instrument reinitialization.
NOTE: If the tape saver feature is used, the bypass flow must be turned off prior to performing an external flow calibration.

Each 15-m roll of tape provides approximately 1500 spots. Each spot lasts from hours in cities at high BC concentrations to several months at remote locations, so changing the tape roll is required only occasionally. The display screen of the computer shows an estimate of the percentage of the tape roll remaining and provides a warning when the value falls below 10%. The Magee Scientific manual (The Aethalometer™, 2003-04, by A.D.A. Hansen; Magee Scientific Company, Berkeley, CA) provides a thorough description of the tape-changing process.

4.6.4.2 Operating Protocol for Model AE-16-ER Aethalometer™

This protocol addresses performing BC measurements using the Model AE-16-ER Aethalometer™ with a 5-Lpm BGI "Photometer" Cyclone (Model 1.829) $PM_{2.5}$ inlet for the NATTS Program. The instrument is operated with the default values except for the following:

- the sample flow is set to 5 Lpm;
- the timebase is set to 5 minutes; and
- the temperature is set at 25°C (versus the instrument default of 20°C).

4.6.4.3 Site Maintenance and QC procedures

The following procedure has been adapted from that prepared by the Harvard School of Public Health, April 1999 (George Allen) and included in the Appendix of the Magee Scientific Aethalometer™ User Manual 2003.04 available at www.mageesci.com.. This information is provided as a starting point for the development of site-specific maintenance and QC procedures.

Daily or Every Site Visit:

- Check the Aethalometer™ display for normal operation (reasonable readings for time and flows, no error messages, error lights, etc.).

Once Each Week:

- Check system date and time on the Aethalometer™ display and on the data logger (if used). The Aethalometer™ time should be within 1 minute of the site's master time source. If the time is reset, record the time error before changing the time, and the date and time you changed the time. The Aethalometer™ must be "stopped" to change the time. A security code must be entered to stop the Aethalometer™ and perform certain other system operating tasks; the default code is 111 and should not be changed. If there is a clear trend in the system time error (for example, a system typically might gain 1 min each week), set the time somewhat off in the opposite direction of the trend to reduce the need for frequent system time changes.

- Check the sample flow on the Aethalometer™ display and record it in the log. The sample flow should be 5.0 ± 0.3 Lpm. Adjust sample flow if necessary, and record the adjusted value in the log sheet.

- Check the filter tape supply. Change filter tape if the thickness of the roll is less than 1/8 in. Re-tension the tape roll takeup spool if needed. Inspect the used filter tape spots that are visible for distinct and uniform borders between the exposed and unexposed areas. If obvious poor seals are noted, contact Magee Scientific.

Once Each Month:

- Clean the cylone once each month.

- While the Aethalometer™ is in its normal run mode, perform an external flow check. Do not stop data collection on the Aethalometer™ to do this test, since stopping data

collection can change the flows. Note: The tape saver function must be off to perform this flow check procedure.

- Measure the sample flow at the inlet of the cylone using a BIOS flow meter, dry test meter, rotameter, or other calibrated volumetric (e.g., not standard temperature and pressure (STP)) flow measurement device with a range of 3 to 8 Lpm. Wet flow devices are not recommended because they cannot be used below freezing and often have a relative humidity-dependent error due to water vapor. The external flow meter must be at ambient temperature for readings to be valid. An STP flow device can be used if the temperature is within 5°C of 25°C; in this case skip the next step.

- Record the flow from the Aethalometer™ display. Correct the external volumetric flow measurement to standard conditions of 25°C and 29.92 inches Hg as follows:

  STP flow = actual flow * [298/(273 + ambient T, °C)] * [station BP, in./29.92]

- Calculate the percent error of the Aethalometer™ flow compared to the external flow standard.

  % error = 100 * (Aethalometer™ display - external STP flow) / external STP flow

- If the flow difference is more than 7%, corrective action may be necessary.

- Leak check the Aethalometer™ by disconnecting the inlet hose at the rear of the instrument and blocking the inlet on the back. In order for this check to work properly, it must be done in the sig and flows menu. In addition, ensure that the unit is not in the bypas test mode and that the minimun (not the final) flow is recorded. The lowest flow reading observed on the flow meter display should be less than 2.5 Lpm. Reconnect the sample line.

- Change the Aethalometer™ data disk. The Aethalometer™ does not need to be interrupted to change the data disk as long as the change is done during the first 3 min of any 5-min measurement cycle [based on the Aethalometer™'s internal clock]. Before changing the disk, start by labeling a new disk with the site and start date/time (local standard time). Remove the old data disk and insert the new disk. Immediately put the write protect tab on the old disk, and record the end date/time (Standard Time) on the disk label. Return the disk to the central laboratory.

<u>Operational Issues and Options:</u>

- Tape Saver: Use of the tape saver option results in a 2.5-fold increase in spot life; however, it makes flow checks more complex.

- Failure to Advance: To avoid the failure to advance error, set the ‘spots per advance’ option to 2 rather than 1.

- Tape Change: For each filter-tape change, the stainless steel filter support mesh screen should be cleaned. Remove the locking screws attaching the top of the inlet cylinder to the lifting plate, and carefully lift it up and away from the base. Clean any accumulation of quartz fiber from the top of the mesh screen When replacing the inlet cylinder, check carefully that it is properly seated on the base.

- Optical sampling and analysis cylinder: This should be cleaned once every year or two or at any time there is the possibility that foreign material such as insects, macroscopic dust, or filter matter has been drawn into the cylinder. This may need to be done more frequently in areas with high aerosol concentrations. A good guideline is to perform the cleaning every second time a roll of tape is installed. The disassembly and cleaning procedure takes less than 30 minutes, requires no special tools and the instrument may be reassembled without concern about critical alignment or repositioning of components. A detailed procedure is supplied in the Aethalometer™ manual.

An example field data sheet is provided in Figure 4.6-1.

Aethalometer™ Instrument
Field Data Sheet

Site Name:_____ Magee Scientific AE-____ Serial #:_____ Date:_____

Weekly Checks:	**Week 1**	**Week 2**	**Week 3**	**Week 4**
Actual Date, Time				
Inst. Date, Time				
Time reset: (min)				
Green Light (**T**)				
Flow (sLpm)				
Tape Supply (**T**)				
Tape Tension (**T**)				
Filter Seals (**T**)				
Clean Inlet, Date				
Operator Initials				

Operator Comments:_____
_____
_____

Monthly Check: Date:_____ Operator Initials:_____
Configuration: Compare to Printed Message Text Log. Inst. settings correct? Y/N_____

Flow Check: (Audit device Serial #:_____ Flow: sLpm_____) (Flow:_____)

(Flow measurement can be performed inside)Flow at 5 sLpm Y/N: _____

Leak Check: (Block inlet on rear of Inst. for 30 seconds.) Less than 2.5 (Lpm) Y/N: _____

Change Data Diskette: Do this during first 3 minutes of 5-min cycle. Label diskette with site and data date range. Write protect and send diskette back to central office.
Note: flow standard conditions are T = 25°C and P = 1013 mbar

Note: Inspect recent collection areas on tape for sharp definition indicating a good filter seal.

Figure 4.6-1. Example of a Field Data Sheet for Aethalometer™ Measurements

4.6.5 Validation

The only check available is to validate the response of the air mass flow meter that monitors the sample flow rate. If there is concern about stability of the optical subsystem, the sensor and reference channel voltages on a clear filter spot can be compared to those reported on the data sheet shipped with the instrument using the optical test strip provided with the Aethalometer™.

The hourly data completeness has been set to 75% for the Aethalometer™ BC data. This is a deviation from the 85% completeness set for other the priority air toxics pollutants in order to accomodate the missed data expected with the automatic tape advance feature of the instrument. Nine 5-minute measurements are required for a valid 1-hour value. The daily completeness has also been set to 75%. Eighteen out of 24 hourly values are needed for a complete day.

4.6.6 Accuracy/Sensitivity

Sensitivity is proportional to sample airflow rate and inversely proportional to the integrating timebase. At typical conditions (5 Lpm flow, 5 minutes timebase), the typical noise level is <0.1 : g/m^3. Data can be generated at short timebases and then averaged over longer periods to recover higher sensitivity equivalent to longer integrating times. The timebase should always be set to 5 minutes. Accuracy is determined by accuracy of airflow meter, typically 2%. Absolute relationship to chemical determination of BC on collocated filter samples depends upon chemical method and aerosol composition.

4.6.7 Data Processing

Data processing software has been developed by the Air Quality Laboratory at Washington University in St. Louis in collaboration with (Northeast States for Coordinated Air Use Management (NESCAUM)) to postprocess the raw data files obtained directly from the Aethalometer™. This program can process data from 1- or 2-channel configurations of the Aethalometer™. At the writing of this document, the software is in 'beta testing'.

Raw data are obtained from the Aethalometer™ in 5-min intervals and stored onto a floppy disk or other acquisition device. The Washington University/NESCAUM program uses the raw data file(s) as input and generates two processed data files as output: 1) a 5-min data output file (similar to the raw data file but with additional formatting and data validation); and 2) a 1-hour average output file, which also includes data validation. Both output files are in comma-delimited format which can easily be imported into spreadsheets or other data analysis packages. BC concentrations are reported as ng/m^3 in the raw data files and : g/m^3 in the postprocessed output files. A log file is also generated which provides important documentation concerning the postprocessing.

The maximum file size that can be processed is determined by the number of 5-min intervals between the two extreme time stamps in the input file. At this time, the software can handle up 133 days or about 4 months worth of data files. The processor cannot handle time stamps prior to January 1, 2000. This software is expected to be available to the public in the near future.

4.7 OVERVIEW OF METEOROLOGICAL MONITORING

This section provides general guidance for:

- In situ monitoring of primary meteorological variables determined by direct measurement: wind direction, wind speed, temperature, relative humidity, precipitation, barometric pressure, and solar radiation;
- Remote sensing of winds and temperature; and
- Derived meteorological variables such as stability, mixing height, and turbulence.

Primary meteorological variables with measurement requirements are shown in Table 4.7-1.

Table 4.7-1. Overview of Meteorological Monitoring Requirements

Question	Answer	
Where to monitor?	At the NATTS Program site, or at a representative site selected in an area network (i.e., if there is more than one NATTS Program site in the same general area). An upper-air monitoring site representative of each NATTS site would be desirable.	
When to monitor?	Routine continuous monitoring	
What parameters?	Wind Direction Wind Speed Air Temperature Dew Point[1]	Solar Radiation Barometric Pressure Precipitation Relative Humidity[1]
What interval?	Surface measurements should be continuous and should be reported hourly. Upper-air measurements (profiles of wind and temperature) should be made at least 4 times/day.	
What levels?	Surface measurements should be made at 2 m (temperature and humidity) or 10 m (wind direction and wind speed). Other surface measurements are nominally made at about 2 m.	

[1] Accuracy not applicable at extreme humidities (<10% or >95% relative humidity).

Detailed guidance for meteorological monitoring is available through the EPA document, "Meteorological Monitoring Guidance for Regulatory Modeling Applications."[39] Recommended procedures for quality assurance and audit activities for the meteorological monitoring system are found in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements*.[40]

Meteorology is a critical element in the formation, transport, and ultimate disposition of many pollutants. Consequently, meteorological data are essential to the development and evaluation of control strategies and the assessment of trends. Other types of evaluations that depend on meteorological data include modeling, diagnostic analysis, emissions trading, and health effects analysis. In support of NATTS, meteorological monitoring must address the parameters presented in Table 4.7-1.

4.7.1 System Specifications for Meteorological Measurements

System specifications for the measurements are shown in Table 4.7-2. The data acquisition system should sample the meteorological sensors at 10-second intervals. Data for all variables should be processed to obtain 1-hour averages. The data acquisition system clock should have an accuracy of ±1 minute per week.

Table 4.7-2. System Specifications for Surface Meteorological Measurements[1]

Variable	Range	Accuracy	Resolution	Time/Distance Constants
Wind Speed	0.5 - 50 m/s	±0.2 m/s + 5%	0.1 m/s	5 m (63% response)
Wind Direction	0 - 360°	±5°	1°	5 m (50% recovery)
Air Temperature	-20 - 40°C	±0.5°C	0.1°C	60 seconds (63% response)

(Continued)

Table 4.7-2. (Continued)

Variable	Range	Accuracy	Resolution	Time/Distance Constants
Dew Point[2]	-30 - +30°C	±1.5°C	0.1°C	30 min
Relative Humidity[2]	0 - 100% RH	±3% RH ±5% RH @ >90% RH	0.5% RH	60 seconds (63% response)
Solar Radiation	0 - 1200 W m^{-2}	±5%	10 W m^{-2}	60 seconds (99% response)
Barometric Pressure	800 - 1100 hPa	±3 hPa	0.5 hPa	60 seconds (63% response)
Precipitation	0 - 30 mm/hour	±10%	0.25 mm	60 seconds (63% response)

[1]Quality assurance guidance for auditing these values is provided in *Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV, Meteorological Measurements*. EPA/600/R-94/038d. U.S. Environmental Protection Agency, 1995.
[2]Accuracy not applicable at extreme humidities (<10% or >95% relative humidity).

4.7.1.1 Siting Considerations

Surface meteorological measurements for the NATTS Program should be made at the NATTS Program site where practical. For general application, the site should be located in a level, open area away from the influence of obstructions such as buildings or trees. The area surrounding the site should have uniform surface characteristics.[41] Although it may be desirable to collocate the surface meteorological measurements with the ambient air quality measurements, collocation of the two functions may not be possible at all monitoring sites without violating one or more of the above criteria. Siting and exposure requirements specific to each of the surface meteorological variables are discussed in subsequent sections.

Surface meteorological measurements in urban areas present special difficulties because compliance with siting and exposure criteria may be precluded by the close proximity of buildings and other structures. In all cases, specific site characteristics should be well documented, especially where surface characteristics and/or terrain are not uniform and when standard exposure and siting criteria cannot be met.

As a general rule, meteorological sensors should be sited at a distance beyond the influence of obstructions such as buildings and trees. This distance depends on the variable being measured as well as the type of obstruction. Another general rule is that meteorological measurements should be representative of the type of meteorological conditions in the area of interest. However, a quantitative method does not exist for determining meteorological representativeness absolutely—there are no generally accepted analytical or statistical techniques to determine representativeness of meteorological data or monitoring sites. Representativeness has been defined as "the extent to which a set of measurements taken in a space-time domain reflects the actual conditions in the same or different space-time domain taken on a scale appropriate for a specific application."[42] For use in air quality modeling applications, meteorological data should be representative of conditions affecting the transport and dispersion of pollutants in the area of interest as determined by the locations of the sources and receptors being modeled. In many instances, multiple meteorological monitoring sites may be required to adequately represent spatial variations. In selecting monitoring sites, secondary considerations such as accessibility and security must be considered but cannot be allowed to compromise the quality of the meteorological data. In addition to routine maintenance and quality assurance activities, annual site inspections should be performed to verify the siting and exposure of the sensors.

Wind instruments must be placed while taking into account the purpose of the measurements. The instruments should be located over level, open terrain at a height of 10 m above the ground and at a distance of at least ten times the height of any nearby obstruction.

Complex terrain refers to any site where terrain effects on meteorological measurements may be significant. Terrain effects include aerodynamic wakes, density-driven slope flows, channeling, flow accelerations over the crest of terrain features, etc. These flows primarily affect wind speed and wind direction, but temperature and humidity measurements may also be affected. A siting decision in complex terrain will almost always represent a compromise. Monitoring options in complex terrain range from a single tall tower to multiple tall towers supplemented by data from one or more remote sensing platforms. Since each complex terrain situation has unique

features, no specific recommendations will cover all cases. However, the recommended steps in the siting process are relevant to all situations:

- Define the variables needed for the specific application.
- Develop as much information as possible to assess what terrain influences are likely to be important: examine topographic maps, estimate plume rise, and analyze any available site-specific meteorological data. An evaluation by a meteorologist based on a site visit would be desirable.
- Examine alternative measurement locations and techniques while considering advantages and disadvantages of each technique/location.
- Optimize network design by balancing advantages and disadvantages.

Guidance and concerns specific to the measurement of wind speed, wind direction, and temperature difference in complex terrain are addressed in the EPA guidance document.[39]

Coastal locations feature unique meteorological conditions associated with local scale land-sea breeze circulations. To provide representative measurements for the entire area of interest, multiple meteorological monitoring sites are needed: one site at a shoreline location and additional inland sites perpendicular to the orientation of the shoreline. Where terrain in the vicinity of the shoreline is complex, measurements at additional locations such as bluff tops may also be necessary.

Urban areas are characterized by increased heat flux and surface roughness, effects that vary horizontally and vertically within the urban area and alter the wind pattern relative to the outlying rural areas. Close proximity of buildings in downtown urban areas often precludes strict compliance with standard sensor exposure guidance. In general, multiple sites are needed to provide representative measurements in a large urban area, especially true for ground-level sources where low-level local influences such as street canyon effects are important and for multiple elevated sources scattered over an urban area.

4.7.1.2 Wind Speed and Wind Direction

Wind speed determines the amount of initial dilution experienced by a plume and is used in the calculation of plume rise associated with point source releases. Wind speed and wind direction are essential to the evaluation of transport and dispersion processes of all atmospheric pollutants. Wind speed is typically measured with mechanical sensors (cup or propeller anemometers) or nonmechanical sensors (hot wire anemometers and sonic anemometers). The nonmechanical sensors are not addressed in the EPA guidance, but their use is not precluded if prior EPA approval is obtained. Wind direction for meteorological purposes (defined as the direction from which the wind is blowing) is typically measured with a wind vane and configured to indicate degrees clockwise from true north.

The standard height for surface layer wind measurements is 10 m above ground level.[40] The location of the site for wind measurements should ensure that the horizontal distance to obstructions (e.g., buildings, trees, etc.) is at least ten times the height of the obstruction. In urban areas (where the "ten times" criterion may not be met), a protocol should be provided to invalidate the measurements for the problem directions. Evans et al.[41] provide a discussion of the validity of 10-m wind data in an urban setting where the average obstruction height is of the same order as the wind measurement height.

An open-lattice tower is the recommended structure for monitoring of meteorological variables at the 10-m level. In the case of wind measurements, certain precautions are necessary to ensure that the measurements are not significantly altered by turbulence in the immediate wake of the meteorological tower. To avoid such tower effects, the wind sensor should be mounted on a mast a distance of at least one tower width above the top of the tower or, if the tower is higher than 10 m, on a boom projecting horizontally from the tower. In the latter case, the boom should extend a distance at least twice the diameter/diagonal of the tower from the nearest point on the tower. The boom should project into the direction that provides the least distortion for the most important wind direction (i.e., into the prevailing wind).

There are several types of open-lattice towers: fixed, tilt-over, and telescopic. A fixed tower is usually assembled as a 1-piece structure from several smaller sections. This type of tower must be sturdy enough to be climbed safely to install and service the instruments. Tilt-over

towers are also 1-piece structures but are hinged at ground level. This type of tower has the advantage of allowing the instruments to be serviced at ground level. Telescopic, 10-m towers are usually composed of three sections, each approximately 4 m in length. The top section is the smallest in diameter and fits inside the middle section which in turn fits inside the base section. The tower can be extended to a height of 10 m by use of a hand crank located at the lowest section. The top of the tower can be lowered to a height of about 4 m to provide easy access to the wind sensors. Telescopic and tilt-over towers are not generally recommended for heights above 10 m. Regardless of which type of tower is used, the structure should be sufficiently rigid and properly guyed to ensure that the instruments maintain a fixed orientation at all times. Instrumentation for monitoring wind speed and direction should never be mounted on or near solid structures, such as buildings, stacks, water storage tanks, cooling towers, etc., because all such structures create significant distortions in the flow field.

A sensor with a high accuracy at low wind speeds and a low starting threshold is recommended for ambient monitoring applications. Lightweight materials (e.g., molded plastic or polystyrene foam) should be used for cups and propeller blades to achieve a starting threshold (lowest speed at which a rotating anemometer starts and continues to turn and produce a measurable signal when mounted in its normal position) of # 0.5 m s^{-1}. Wind vanes or tail fins should also be constructed from lightweight materials. The starting threshold (lowest speed at which a vane will turn to within 5 degrees of the true wind direction from an initial displacement of 10 degrees) should be #0.5 m s^{-1}. Overshoot must be # 25% and the damping ratio should lie between 0.4 and 0.7.

4.7.1.3 Temperature

Temperature affects photochemical reaction rates and consequently is an essential variable for ambient monitoring applications. Sensors used to monitor ambient temperature include wire bobbins, thermocouples, and thermistors. Platinum resistance temperature detectors (RTD) are among the more popular sensors used in ambient monitoring. These sensors provide accurate measurements and maintain a stable calibration over a wide temperature range. The RTD operates

on the basis of the resistance changes of certain metals, usually platinum or copper, as a function of temperature. Thermoelectric sensors (called thermocouples) work on the principle of a temperature-dependent electrical current flow between two dissimilar metals. Thermocouples are susceptible to induction currents generated from nearby AC sources as well as spurious voltages caused by moisture, so their usefulness for routine field measurements is limited.

The standard height for surface layer ambient temperature measurements is 2 m above ground level.[42,43] If a tower is used, the temperature sensor should be mounted on a boom that extends at least one tower width/diameter from the tower. The measurement should be made over a uniform plot of open, level ground at least 9 m in diameter. The surface should be covered with nonirrigated or unwatered short grass or, in areas which lack a vegetation cover, natural earth. Concrete, asphalt, and oil-soaked surfaces and similar surfaces should be avoided to the extent possible. The sensor should be at least 30 m from any paved area. Other areas to avoid include large industrial heat sources, roof tops, steep slopes, hollows, high vegetation, swamps, snow drifts, standing water, and air exhausts. The distance to obstructions for accurate temperature measurements should be at least four times the obstruction height. In urban areas, extraneous energy sources (e.g., tunnels and subway entrances, roof tops, etc.) should be very deliberately avoided.

Temperature measurements should be accurate to ± 0.5°C over a range of -20 to +40°C with a resolution of 0.1°C. The time constant (63.2%) should be # 60 seconds. Solar heating is usually the greatest source of error; consequently, adequate shielding is needed to provide a representative ambient air temperature measurement. Ideally, the radiation shield should block the sensor from view of the sun, sky, ground, and surrounding objects. The shield should reflect all incident radiation and not reradiate any of that energy toward the sensor. A forced aspiration shield is needed for temperature/relative humidity measurements at 2 m. The best type of shield provides forced aspiration at a rate of at least 3 m s^{-1} over a radiation range of -100 to +1100 W m^{-2}. Errors in temperature should not exceed ±0.25°C when a sensor is placed inside a forced aspiration radiation shield. The sensor must be protected from precipitation and condensation; otherwise evaporative effects and other forms of radiational heating or cooling will

lead to a depressed temperature measurement (i.e., wet bulb temperature). Temperatures may also be reported to EPA's AQS in °F, but metric is the preferred and recommended system of units for meteorological measurements.

4.7.1.4 Atmospheric Humidity

Humidity is a general term related to the amount of moisture in the air. Variables related to humidity include vapor pressure, dew point temperature, specific humidity, absolute humidity, and relative humidity. Measurements of atmospheric humidity are essential to understanding chemical reactions involving air pollutants and water vapor. There are several ways to measure the water vapor content of the atmosphere. The classical measurement methods can be classified in terms of six scientific principles, as shown in Table 4.7-3.

The standard height for humidity measurements is 2 m above ground level. The humidity sensor should be installed using the same siting criteria used for temperature. If possible, the humidity sensor should be housed in the same aspirated radiation shield as the temperature sensor. The humidity sensor should be protected from contaminants such as salt, hydrocarbons, and other particulate materials. The best protection is the use of a porous membrane filter, which allows the passage of ambient air and water vapor while keeping out particulate matter.

Table 4.7-3. Principles of Humidity Measurement[1]

Principle	Instrument/Method for Implementation
Reduction of temperature by evaporation	Psychrometer consisting of two thermometers, one covered with a wet wick with a mechanism for ventilating the pair. Evaporation lowers the temperature of the wet bulb; the difference in temperature from the dry bulb is a measure of the moisture in the air. Psychrometers are generally not suitable for routine monitoring programs.
Dimensional changes due to absorption of moisture, based on hygroscopic properties of materials	Hygrometers with sensors of hair, wood, natural and synthetic fibers
Chemical or electrical changes due to absorption or adsorption	Electric hygrometers such as the Dunmore Call; lithium, carbon, and aluminum oxide strips; capacitance film
Formation of dew or frost by artificial cooling	Cooled mirror surfaces
Diffusion of moisture through porous membranes	Diffusion hygrometers
Adsorption spectra of water vapor	IR and UV absorption: Lyman-alpha radiation hygrometers

[1]Middleton, W.E.K., and Spillhaus, A.F. *Meteorological Instruments*, University of Toronto Press (1953).

4.7.1.5 Precipitation

Precipitation data are used for consistency checks in data review and validation. Precipitation measuring devices include the tipping bucket rain gauge and the weighing rain gauge. Both types of gauge measure total liquid precipitation and may also be used to measure the precipitation rate, but the tipping bucket is preferable for that application. The tipping bucket rain gauge is probably the most common type of instrument in use for meteorological programs; a single and multitip test must be performed with the tipping bucket. The rain gauge should be located on level ground in an open area. Obstructions should not be closer to the instrument than two to four times their height. The area around the rain gauge should be covered with natural vegetation. The mouth of the rain gauge should be level and should be as low as possible but still precluding in-splashing from the ground (30 cm above ground level is the recommended minimum height). A

wind shield/wind screen (such as an Alter-type wind shield, consisting of a ring with approximately 32 free-swinging, separate metal leaves) should be used to minimize the effects of high wind speeds.

4.7.1.6 Solar Radiation

Solar radiation refers to the electromagnetic energy in the solar spectrum (0.10 - 4.0 :m wavelength). The latter is commonly classified as UV (0.10 - 0.40 :m), visible light (0.40 - 0.73 :m), and near-IR (0.73 - 4.0 :m) radiation. About 97% of the solar radiation reaching the outer atmosphere of earth lies between 0.29 and 3.0 :m.[43] A portion of this energy penetrates through the atmosphere and is either absorbed or reflected at the surface of the earth. The rest of the solar radiation is scattered and/or absorbed in the atmosphere before reaching the surface of the earth. Solar radiation measurements are used in heat flux calculations that estimate atmospheric stability and in modeling photochemical reactions.

Energy fluxes in the spectrum of solar radiation are measured using a pyranometer. These instruments are configured to measure what is referred to as global solar radiation (i.e., direct plus diffuse (scattered) solar radiation). The sensing element of the typical pyranometer is protected by a clear glass dome to prevent entry of energy (wavelengths) outside the solar spectrum (i.e., long-wave radiation). The glass domes used on typical pyranometers are transparent to wavelengths in the range of 0.28 - 2.8 :m.

Solar radiation measurements should be taken in a location with an unrestricted view of the sky in all directions. In general, locations should be avoided that have obstructions which could cast a shadow or reflect light on the sensor; light-colored walls or artificial sources of radiation should also be avoided. The horizon as viewed from the pyranometer should not exceed 5 degrees. Sensor height is not critical for pyranometers. Consequently, tall platforms or rooftops are typical locations. Regardless of where the pyranometer is sited, it is important to ensure that the level of the instrument is maintained and that the glass dome is cleaned as necessary.[44] To facilitate leveling, the pyranometers should be equipped with an attached circular spirit level.

Manufacturer's specifications should match the requirements of the World Meteorological Organization for either a secondary standard or first class pyranometer (see Table 4.7-4), especially if the measurements are to be used for estimating heat flux.[43] Photovoltaic pyranometers (which usually fall under second class pyranometers) may be used for ambient air monitoring applications on a case-by-case basis. The cost of photovoltaic-type sensors is significantly less than the cost of thermocouple-type sensors. However, their spectral response is limited to the visible spectrum. An Eppley precision spectral pyranometer (PSP) is the best instrument to measure global solar radiation due to a better cosine response, but a thermopile sensor should be used instead of a Licor silicon cell.

Table 4.7-4. Classification of Pyranometers[1]

Characteristic	Units	Secondary Standard	First Class	Second Class
Resolution	W m^{-2}	±1	±5	±10
Stability	%FS $year^{-1}$	±1	±2	±10
Cosine Response	%	< ±3	< ±7	< ±15
Azimuth Response	%	< ±3	< ±5	< ±10
Temperature Response	%	±1	±2	±5
Nonlinearity	%FS	±0.5	±2	±5
Spectral Sensitivity	%	±2	±5	±10
Response Time (99%)	seconds	< 25	< 60	< 240

[1]Quality Assurance guidance for auditing these parameters is provided in *Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV, Meteorological Measurements*. EPA/600/R-94/038d. U. S. Environmental Protection Agency, 1995.

4.7.1.7 Barometric Pressure

Barometric pressure (station pressure) is used in all calculations of fundamental thermodynamic quantities (e.g., air density). There are two basic types of instruments available for measuring atmospheric pressure: the mercury barometer and the aneroid barometer. The Hg barometer measures the height of a column of mercury supported by the atmospheric pressure but does not offer the convenience of automated data recording. An aneroid barometer uses a pressure transducer as a sensor. There are numerous commercially available pressure transducers that meet specifications for a monitoring program; values can be recorded either in the analog or digital mode. Ideally, the pressure sensor should be located in a ventilated shelter about 2 m above ground level. The height of the station above mean sea level and the height of the pressure sensor above ground level should be documented. If needed, the pressure can then be adjusted to standard height. An aneroid or pressure transducer is needed to measure station barometric pressure.

If the pressure sensor is placed indoors, accommodations should be made to vent the pressure port to the outside environment. One end of a tube should be attached to the pressure port of the sensor, and the other end should be vented to the outside of the trailer or shelter so that pressurization due to the air-conditioning or heating system is avoided. The wind can often cause dynamic changes of pressure in a room in which a sensor is placed. These fluctuations may be on the order of 2 - 3 hPa when strong or gusty winds prevail.

4.7.1.8 System Performance

Accuracy is the amount by which a measured variable deviates from a value accepted as true or standard. The accuracy of a measurement system can be estimated if the accuracies of the individual components are known. Accuracies recommended for meteorological monitoring systems are shown in Table 4.7-5, stated in terms of overall system accuracy since the data from the measurement system are used in air quality modeling analyses. Recommended measurement

Table 4.7-5. Recommended System Accuracy and Resolution[1]

Meteorological Variable	System Accuracy	Measurement Resolution
Wind Speed (horizontal and vertical)	± (0.2 m/s + 5% of observed)	0.1 m/s
Wind Direction (azimuth and elevation)	±5 degrees	1.0 degree
Ambient Temperature	±0.5°C	0.1°C
Vertical Temperature Difference	±0.1°C	0.02°C
Dew Point Temperature	±1.5°C	0.1°C
Precipitation	±10% of observed or ±0.5 mm	0.3 mm
Pressure	±3 mb (0.2 kPa)	0.5 mb
Solar Radiation	±5% of observed	10 W/m^2

[1]These recommendations are applicable to microprocessor-based digital systems as the primary measurement system. For analog systems used as backup, these recommendations may be relaxed by 50%.

resolutions (i.e., the smallest increments that can be distinguished) are also shown in Table 4.7-5. These resolutions are considered necessary to maintain the recommended accuracies and are required in the case of wind speed and wind direction for calculation of standard deviations.

The response characteristics of the sensors used for meteorological monitoring must be known to ensure that data are appropriate for the intended application. Definition of terms and recommended response characteristics for meteorological sensors used in support of air quality monitoring are discussed in detail in EPA's guidance document.[39] Manufacturer's documentation verifying the response characteristics of an instrument should be reviewed to ensure that verification tests have been conducted in a laboratory setting according to accepted scientific/technical methods.

Data bases for use in regulatory dispersion modeling applications should be 90% complete (before substitution). The 90% requirement applies to each meteorological variable separately and to the joint recovery of wind direction, wind speed and stability. Compliance with the 90% requirement should be evaluated on a quarterly basis.

4.7.2 Upper-Air Meteorological Monitoring

The most widely used technologies for monitoring upper-air meteorological conditions include radiosondes and ground-based remote sensing platforms including sodar (sound detection and ranging), radar (radio detection and ranging), and radio acoustic sounding system (RASS). The design of a program for performing upper-air monitoring will depend upon region-specific factors. The optimal design for a given region is expected to be some combination of remote sensing and conventional atmospheric soundings. In special cases, the upper-air monitoring plan may be augmented with data from aircraft and/or tall towers. Data from existing sources (e.g., the National Weather Service (NWS) upper-air network) should be considered and integrated with the ambient air trends monitoring plan. Site selection is extremely critical for a boundary layer wind profiler and sodar system. Ambient noise considerations and tall obstructions will affect sodar measurements.

Upper-air wind speeds and wind directions are vector-averaged measurements. Remote sensing systems (e.g., Doppler sodar) provide continuous measurements of wind speed and wind direction as a function of height. These data are needed to provide wind data with the necessary temporal and vertical resolution to evaluate changes in transport flow fields coincident with the evolution of the convective boundary layer. Such evaluations can aid in the diagnosis of conditions associated with extreme ozone concentrations, for example. The capabilities of the various platforms for upper-air meteorological monitoring (towers, balloon systems, and remote sensors) are compared in Table 4.7-6.

Table 4.7-6. Capabilities and Limitations of Meteorological Measurement Systems for Vertical Profiling of the Lower Atmosphere

Variable	Tower	Sodar[3]	Mini-sodar	Radar	Radar with RASS	Radiosonde	Tethersonde
	Typical Maximum Height/Range (m above ground level)						
Wind Speed	100[1]	600	300	2 - 3 km	2 - 3 km	>10 km	1000
Wind Direction	100[1]	600	300	2 - 3 km	2 - 3 km	> 10 km	1000
Wind Sigmas[2]	100[1]	600	300	2 - 3 km	2 - 3 km	NM	NM
Relative Humidity	100[1]	NM	NM	NM	NM	> 10 km	1000
Temperature	100[1]	NM	NM	NM	1.2 km	> 10 km	1000
	Typical Minimum Height (m above ground level)						
Wind Speed	10	50	10	100	100	10	10
Wind Direction	10	50	10	100	100	10	10
Wind Sigmas[2]	10	50	10	100	100	NM	NM
Relative Humidity	2	NM	NM	NM	NM	10	10
Temperature	2	NM	NM	NM	100	10	10
	Typical Resolution (m)						
Wind Speed	2 - 10	25	10	60 - 100	60 - 100	5 - 10	10
Wind Sigmas[2]	2 - 10	25	10	60 - 100	60 - 100	NM	NM
Relative Humidity	2 - 10	NM	NM	NM	NM	5 - 10	10
Temperature	2 - 10	NM	NM	NM	60 - 100	5 - 10	10

NM = Not measured; no capability for this variable.
[1]Typically meteorological towers do not exceed 100 m. However, radio and TV towers may exceed 600 m.
[2]The standard deviation of horizontal and vertical wind components.
[3]The sodar system antenna must be properly oriented with respect to true north, and 10 m wind direction must have proper alignment and integrity.

Conventional atmospheric soundings obtained using rawinsondes or their equivalent are needed to provide atmospheric profiles with the necessary vertical resolution for estimating the mixing height and for use in initializing the photochemical grid models used for evaluating control strategies. Such soundings should extend to the top of the convective boundary layer (CBL) or 1000 m, whichever is greater, and should include measurements of wind speed, wind direction, temperature, and humidity. Four soundings per day are needed to adequately characterize the

development of the atmospheric boundary layer. These soundings should be acquired just prior to sunrise when the atmospheric boundary layer is usually the most stable, in mid-morning when the growth of the boundary layer is most rapid, during mid-afternoon when surface temperatures are maximum, and in late afternoon when the boundary layer depth is largest. Soundings obtained from a NWS upper-air station may be used to obtain part of this information depending on the time of the sounding and the location of the NWS site.

4.7.2.1 Siting and Exposure for Upper-Air Measurements

The upper-air measurements are intended for more macro-scale application than are the surface meteorological measurements. Consequently, the location of the upper-air site need not be associated with any particular surface monitoring site. Factors that should be considered in selecting a site for the upper-air monitoring include whether the upper-air measurements for the proposed location are likely to provide the necessary data to characterize the meteorological conditions associated with the parameters of interest, and the extent to which data for the proposed location may augment an existing upper air network. Near lake shores and in coastal areas, where land/sea/lake breeze circulations may play a significant role in pollutant formation and transport, additional upper-air monitoring sites may be needed. This consideration would also apply to areas located in complex terrain. All of the above are necessary components of the DQOs for an upper air monitoring plan.

4.7.2.2 Tall Towers

In some instances it may be possible to use existing towers located in monitoring areas to acquire vertical profiles of atmospheric boundary layer data. Radio and television transmission towers, which may be as tall as 600 m, can be equipped with in situ meteorological sensors at many levels. An advantage to using a tower is the ability to run an unattended data acquisition system. Also, data can normally be collected under all weather conditions. However, the main disadvantage of using a tower is the inability to determine the mixed layer height during most of the day. When moderate to strong convective conditions exist, the mixed layer height easily exceeds

the height of the tallest towers. Another disadvantage is the potentially high cost of maintenance, especially during instances when the instrumentation needs to be accessed for adjustments or repairs.

4.7.2.3 Balloon Systems

Balloon-based systems include rawinsonde (sometimes called radiosonde) and tethersonde systems. The rawinsonde consists of a helium-filled balloon, an instrumental package, a radio transmitter, and a tracking device. The instrument package includes sensors for measuring atmospheric temperature, relative humidity, and barometric pressure. Data from ground-based radar, used to track the balloon, are processed to determine wind speed and direction. Typical specifications for the sensors used in rawinsondes are shown in Table 4.7-7.

Table 4.7-7. Manufacturer's Specifications for Sensors Used in Rawinsondes

Sensor	Range	Accuracy	Resolution
Pressure	1080 to 3 mb	±0.5 mb	0.1 mb
Temperature	-90° to +60°C	±0.2°C	0.1°C
Relative Humidity	5 - 100%		

Unlike surface measurements, there is no equivalent to system accuracy for upper-air meteorological measurements from rawinsondes. Consequently, to assess the quality of rawinsonde measurements, the NWS uses a special statistical parameter called the "functional precision," defined as the root-mean-square (rms) difference between measurements made by identical instruments at as nearly as possible the same time and same point in the atmosphere[45]. The functional precision of NWS radiosonde measurements is shown in Table 4.7-8.

Table 4.7-8. Functional Precision of Rawinsonde Measurements[45]

Variable	Functional Precision
Wind Speed (at the same height)	± 3.1 m/s
Wind Direction (at the same height)	±18 degrees [# 3.1 m/s] ±14 degrees [5.1 m/s] ±9 degrees [10.3 m/s] ±6 degrees [15.4 m/s] ±5 degrees [20.6 m/s]
Temperature (at the same pressure)	±0.6°C
Dew Point Depression (at the same pressure)	±3.3°C
Height (at the same pressure)	±24 m

A tethersonde system is comprised of a tethered balloon with one or more instrument packages attached to the tether. The instrument package includes a radio transmitter and sensors to measure atmospheric temperature, relative humidity, barometric pressure, wind speed, and wind direction. Data are telemetered to the ground by radio or by conductors incorporated within the tethering cable. Tethersondes are capable of providing data up to about 1000 m in good conditions. Use of a tethersonde is limited by wind speed; they can be used reliably only in light-to-moderate wind conditions (5 m/s at the surface to 15 m/s aloft). Tethered balloons are also considered a hazard to aviation and thus are subject to Federal Aviation Administration (FAA) regulations. A permit is required to operate such a system. A tethersonde system is an excellent way to conduct a performance check on PAI-LR under proper meteorological conditions. The tethersonde provides a check on 15-min average wind speed and wind direction. Sodar PAI-LR measures from 100 m to 2000 m above ground level.

4.7.2.4 Ground-Based Remote Sensors

Ground-based remote sensors have become effective tools for acquiring upper-air information and have played an increasingly important role in atmospheric boundary layer studies. For the NATTS Program, ground-based systems are the preferred approach for upper-air

meteorological monitoring and estimation of mixing heights. There are two basic types of remote sensing systems used to acquire 3-component wind velocity profiles: radar and sodar. Radars (also called wind profilers) transmit an electromagnetic signal (~ 915 megahertz (MHz)) into the atmosphere in a predetermined beam width which is controlled by the configuration of the transmitting antenna. Sodars (also called acoustic sounders) transmit an acoustic signal (~ 2 - 5 kilohertz (KHz)) into the atmosphere in a predetermined beam width, which is also controlled by the transmitting antenna. The radar has a range of approximately 150 - 3000 m with a resolution of 60 - 100 m. The sodar has a range of about 50 - 1500 m with a resolution of about 25 - 50 m.

Both systems transmit their respective signals in pulses. Each pulse is both reflected and absorbed by the atmosphere as it propagates upward. The vertical range of each pulse is determined by how high it can go before the signal becomes so weak that the energy reflected back to the antenna can no longer be detected. As long as the reflected pulses can be discerned from background noise, meaningful wind velocities can be obtained by comparing the Doppler shift of the return signal to that of the output signal. A positive or negative Doppler shift indicates whether the radial wind velocity is moving toward or away from the transmitting antenna. The attenuation of a transmitted pulse is a function of signal type, signal power, signal frequency and atmospheric conditions. Radar signal reflection depends primarily on the presence of an index of refraction gradient in the atmosphere which varies with temperature and humidity. Sodar signal reflection depends primarily on the presence of small-scale atmospheric turbulence. The reflected signals received by either a radar or sodar are processed in a system computer by signal conditioning algorithms.

To obtain a profile of the 3-component wind velocity, one vertical beam and two tilted beams are needed. The two tilted beams are usually between 15 and 30 degrees from the vertical. These two beams are also at right angles to each other in azimuth. For example, one tilted beam may be oriented toward the north while the second tilted beam points east. Each antenna transmits a pulse and then listens for the reflected signal in succession. After all three antennas perform this

function, enough information is available to convert the radial velocities into horizontal and vertical wind velocities by using simple trigonometric relationships.

Radars and sodars may use monostatic or phased array antenna configurations. Monostatic systems consist of three individual transmit/receive antennas. Phased array systems consist of a single antenna array which can electronically steer the beam in the required directions. Vertical panels (also known as clutter fences) are usually placed around the antennas. This placement effectively acts to block any stray side-lobe echoes from contaminating the return signal of a radar. For sodars, these panels cut down on the side-lobe noise, which may be a nuisance to nearby residents and also prevents any background noise that may contaminate the return signal.

A RASS uses a combination of electromagnetic and acoustic pulses to derive a virtual air temperature profile. A RASS usually consists of several acoustic antennas placed around a radar system. The antennas transmit a sweep of acoustic frequencies vertically into the atmosphere. Concurrently, a radar beam is emitted vertically into the atmosphere. The radar beam will most strongly reflect off the sound wave fronts created by the acoustic pulses. The virtual air temperature is computed from the speed of sound which is measured by the reflected radar energy. The typical range of a RASS is approximately 150 - 1500 m with a resolution of 60 - 100 m.

Unlike in situ sensors that measure by direct contact, remote sensors do not disturb the atmosphere. Another fundamental difference is that remote sensors measure a volume of air rather than a fixed point in space. The thickness of the volume is a function of the pulse length and frequency used. The width of the volume is a function of beam spread and altitude. Siting of these profilers is sometimes a difficult task. Artificial and natural objects located near the sensors can potentially interfere with the transmission and return signals, the result of which is corrupted wind velocity data.

Since sodars use sound transmission and reception to determine the overlying wind field, a clear return signal with a sharply defined atmospheric peak frequency is required. Thus,

consideration of background noise may put limitations on where a sodar can be located. External noise sources can be classified as active or passive and as broadband (random frequency) or narrowband (fixed frequency). General background noise is considered active and is broadband. If loud enough, it can cause the sodar software to reject data because it cannot find a peak or because the signal-to-noise ratio is too low. The net effect is to lower the effective sampling rate due to the loss of many transmission pulses. A qualitative survey should be conducted to identify any potential noise sources. A quantitative noise survey may be necessary to determine whether noise levels are within the minimum requirements of the instrumentation.

Examples of active, broadband noise sources include highways, industrial facilities, power plants, and heavy machinery. Some of these noise sources have a pronounced diurnal, weekly or even seasonal pattern. A noise survey should at least cover diurnal and weekly patterns. Examination of land-use patterns and other sources of information may be necessary to determine whether any seasonal activities may present problems.

Examples of active, fixed-frequency noise sources include rotating fans, a backup beeper on a piece of heavy equipment, birds and insects. If these noise sources have a frequency component in the sodar operating range, that frequency component may be misinterpreted as good data by the sodar. Some of these sources can be identified during the site selection process. One approach to reducing the problem of fixed-frequency noise sources is to use a coded pulse (i.e., the transmit pulse has more than one peak frequency). A return pulse would not be identified as data unless peak frequencies were found in the return signal the same distance apart as the transmit frequencies.

Passive noise sources are objects either on or above the ground (e.g., tall towers, power transmission lines, buildings, trees) that can reflect a transmitted pulse back to the sodar antenna. Although most of the acoustic energy is focused in a narrow beam, side-lobes do exist and are a particular concern when antenna enclosures have degraded substantially. Side-lobes reflecting off stationary objects and returning at the same frequency as the transmit pulse may be interpreted by the sodar as a valid atmospheric return with a speed of zero. It is not possible to predict precisely

which objects may be a problem. Anything in the same general direction in which the antenna is pointing and higher than 5 to10 m may be a potential reflector. It is therefore important to construct an "obstacle vista diagram" prior to sodar installation that identifies the direction and height of potential reflectors in relation to the sodar. This diagram can be used after some data have been collected to assess whether or not reflections are of concern at some sodar height ranges. Note that reflections from an object at a distance *X* from an antenna will show up at a height *X*cos ("), where " is the tilt angle of the antenna from the vertical.

The radar, sodar and RASS antennas should be aligned and tilted carefully as small errors in orientation or tilt angle can produce unwanted biases in the data. True north should also be established for antenna alignment. Installation of the antennas should not be permanent since problems are very likely to arise in siting the profilers in relation to the tower and other objects that may be in the area. One final consideration is the effect of the instrument on its surroundings. The sound pulse from a sodar and RASS is quite audible and could become a nuisance to residents who might happen to live near the installation site. This audible pulse should be a consideration in the siting process because of the potential irritation to nearby residents.

4.7.2.5 System Performance

Determining the absolute accuracy of upper air instrumentation through an intercomparison study is difficult because there is no "reference" instrument that can provide a known or true value for the atmospheric conditions due in part to system uncertainties caused by meteorological variability, spatial and temporal separation of the measurements, external and internal interference, and random noise. The only absolute accuracy check that can be performed is on the system electronics, by processing a simulated signal. A true precision, or the standard deviation of a series of measured values about a mean measured reference value, can be calculated only by using the system responses to repeated inputs of the same simulated signal. To quantify the reasonableness of upper-air measurement data, one compares observations from the upper-air system being evaluated to data provided by another sensor that is known to be operating properly. Two measures are commonly used for comparison:

- Calculation of the "systematic difference" between the observed variables measured by the two methods; and
- Calculation of a measure of uncertainty between the measurements, referred to as the "operational comparability."

Details of the calculation process are presented in the EPA guidance document.[240] Other issues addressed in the EPA guidance document include performance characteristics for the various systems, installation and acceptance testing, quality assurance and QC procedures used for the various systems, as well as a discussion of the common problems encountered in upper-air data collection

4.7.3 Estimation of Mixing Height

In addition to the meteorological variables that are measured directly, estimates are also required of the depth of the mixed layer (i.e., mixing height). The mixing height is a derived variable indicating the depth through which vertical mixing of pollutants occurs. Reliable estimates of the mixing height are essential to dispersion modeling. Light detection and ranging (LIDAR) systems are good techniques for determining the mixing height. LIDAR results can be compared to the sodar mixing height (which is derived from an algorithm).

The EPA recommended method for estimating mixing height requires measurement of the vertical temperature profile.[46,47] In this method, the afternoon mixing height is calculated as the height above the ground of the intersection of the dry adiabatic extension of the maximum surface temperature with the 12 a.m. morning temperature profile. This concept of a mixing layer in which the lapse rate is roughly dry adiabatic is well founded on general theoretical principles and on operational use in regulatory dispersion modeling over the last two decades. Comparisons of mixing height estimates based on the Holzworth method with several other techniques indicate that all methods perform similarly in estimating the maximum afternoon mixing depth. The Holzworth method is normally preferred because of its simplicity. Available methods for determining mixing heights are summarized in Table 4.7-9.

Table 4.7-9. Methods Used to Determine Mixing Heights

Platform	Variable Measured	Advantages/Limitations
Aircraft LIDAR	Inert tracer	Consistent with the definition of mixing height as used in dispersion modeling. Labor intensive, not practical for routine applications.
Rawinsonde	Potential temperature	Relatively robust for estimating the daytime (convective) mixing depth. Limited by the noncontinuous nature of rawinsonde launches.
Sodar	Turbulence Acoustic backscatter	For continuous monitoring of boundary layer conditions. Range, however, is limited for sodar; estimates of the mixing height are possible only when the top of the mixed layer is within the range of the sodar. Good for monitoring the nocturnal surface-based temperature inversion—although different from mixing height, nocturnal inversion is equally important for modeling nocturnal dispersion conditions.
Radar wind profiler	Refractive index	For continuous monitoring of boundary layer conditions
RASS	Virtual temperature	Virtual temperature profile obtained using a RASS is used to estimate the convective mixing height in the same way that temperature data are used (limited to the range of the RASS, approximately 1 km).

The mixing height determined with Holzworth's procedure from 00Z and 12Z NWS rawinsonde should be compared with sodar PAI-LR mixing height or RASS or LIDAR mixing height.

4.8 Innovative Methods for Ambient Air Monitoring with Potential for Future Application

This section discusses several innovative methodologies that are potentially applicable to the NATTS network. These methodologies are **NOT** presently accepted by EPA for application to the NATTS Program. Many of them are not documented thoroughly and have not achieved the level of acceptance and recognition that a numbered EPA method confers. Prior EPA approval is required for the use of any of these methodologies in the NATTS Program. The effect on consistency of data resulting from the application of these methods, in place of the accepted NATTS measurement methods, must be assessed.

The prospective user of the alternative methodology must also demonstrate performance equivalent to the currently accepted methodology and produce the necessary documentation (i.e., formally written protocol, SOPs). Specific requirements for demonstrating equivalency of methodology will be defined by EPA. These innovative methods are considered to be nonroutine in nature. Nonroutine methods are more research oriented, more difficult to operate and maintain, and usually require a specially trained or skilled operator. Nonroutine methods may also be new technologies not yet fully field tested or evaluated.

4.8.1 Aldehydes and Ketones

EPA Compendium Method TO-11A[6] has been specifically disqualified for the sampling and analysis of acrolein, a compound of special concern. Extensive development and evaluation of candidate methodologies is therefore being performed to elucidate a methodology that will be effective for the sampling and analysis of acrolein, as well as other carbonyl compounds. One such methodology has been reported by Zhang et al. at Rutgers University featuring the design and evaluation of a tube-type diffusive sampler that uses dansylhydrazine (DNSH)-coated solid sorbent to collect aldehydes and ketones.[48] The derivatized carbonyl compounds are analyzed using a sensitive HPLC-fluorescence technique.

The Rutgers diffusive sampler was evaluated using test atmospheres in the laboratory and was also evaluated in the field where results were compared to the application of the conventional

EPA Compendium TO-11A[6] derivatization method using silica gel sampling cartridges coated with DNPH. The comparative evaluation results indicate that the diffusive sampler is a valid passive sampler for 24 - 48 hour collection of carbonyl compounds in indoor, outdoor or personal air. Use of a passive sampler for outdoor ambient air monitoring has the advantage of removing concerns over the supply of power. Aldehyde/ketone samplers currently employed use DNPH-coated sorbents as the sampling medium for collecting carbonyl compounds as DNPH derivatives (hydrazones). These DNPH derivatives are subsequently extracted and analyzed by HPLC using a UV detector.

The passive sampler reported by the Rutgers team uses a fluorogenic reagent, DNSH, to derivatize the carbonyl compounds. The DNSH derivative has shown enhanced sensitivity and selectivity compared to the DNPH methodology because the DNSH derivatives can be determined using HPLC combined with fluorescence detection, a more sensitive and selective detection method than the UV detection method.

Tubes were prepared for sampling by coating a commercially available C_{18} cartridge with approximately 0.5 mg of DNSH. A dynamic dilution system was used in the laboratory to generate humidified test atmospheres containing formaldehyde, acetaldehyde, propionaldehyde, acrolein, acetone, crotonaldehyde, hexaldehyde and benzaldehyde, compounds selected for testing because of their importance in determining human health risk. When the coated sampling tubes were used to collect ambient air, the tubes were placed in the selected location with the barrel end uncapped and completely exposed. At the end of the sampling period, the barrel end of the sampling cartridge was recapped, the capped sampling tubes were wrapped individually with aluminum foil and placed in a cooler and the tubes were shipped to the laboratory as soon as possible.

Prior to extraction of the derivatized compounds, the capped tubes, wrapped in aluminum foil, were placed in an oven at 60°C for 1 hour to drive the reversible DNSH derivatization reactions in the direction of derivative formation. After the heating period, the cooled tubes were extracted with acetonitrile and analyzed. Extracts were found to be stable under refrigeration at 4°C for at least 7 days; extended time periods have not been tested. The analytical detection limits for the DNSH derivatives from this study ranged from 5 - 26 pg on column, with acrolein showing

a detection limit of 26 pg, as determined by using 3 times the standard deviation from the analysis of acetonitrile extracts of six randomly selected blank, coated sampling cartridges. It has not been determined how this method of determining MDL compares to the procedure using 40 CFR Part 136 Appendix B, so this MDL cannot be compared to the MDLs quoted for EPA Compendium Method TO-11A.[6]

The effects of temperature, relative humidity, face velocity, carbonyl concentrations and sampling duration on the sampling rates were evaluated. A series of experiments was conducted in which the coated sorbent cartridges were exposed to known concentrations of the eight carbonyl compounds in the test atmosphere; recoveries ranged from 60% for acrolein to 107% for propionaldehyde. Relatively low recoveries for acrolein and crotonaldehyde (~76%) were attributed to possible instability of the derivatives.

The performance of the DNSH-coated passively exposed cartridges and actively exposed DNPH cartridges was evaluated comparatively in the field by taking collocated samples on a 48-hour basis. The two methods were shown to agree reasonably well for formaldehyde, acetaldehyde, acetone, and propionaldehyde. On average, the difference between the two methods was within 40% for these four compounds. It is expected that the DNSH-coated tubes can be used outdoors without an O_3 scrubber in high O_3 environments on the basis of a study that found that O_3 (up to 300 ppb) is not a significant interference as long as DNSH is in substantial excess over the carbonyl compounds being derivatized. The O_3 seems to cause only partial oxidation of the DNSH reagent but had no effect on carbonyl-DNSH derivatives.

The use of the DNSH derivative (and of the passive sampling approach) appears to offer some advantages and looks promising for derivatization/analysis of acrolein, but extensive research remains to be performed to determine the range of applicability of the method and comparability to the currently accepted EPA Compendium TO-11A[6] DNPH derivatization method. The preliminary results indicating comparability of the two methodologies for a few compounds to within approximately 40% is not sufficient to demonstrate that the two methods are equivalent. Use of the DNSH derivative in the active sampling mode has not been evaluated, and MDLs have not been determined according to the Federal Register methodology.

4.8.1.1 Application of Modified EPA Compendium TO-11A[6] Methodology to the Analysis of Acrolein and Crotonaldehyde

Analytical procedures as performed in the laboratories of the Texas Commission on Environmental Quality and ERG demonstrate that the DNPH derivatives of both acrolein and crotonaldehyde split into two separate peaks upon HPLC analysis of the extracts because of the formation of two compounds in the derivatization reaction. HPLC retention times for the two acrolein derivative peaks are different, but two distinct chromatographically resolvable peaks are observed. The crotonaldehyde derivative peaks are likewise resolvable. When the two chromatographic peaks obtained for each compound are summed, recovery values for acrolein ranged from approximately 99 - 109%. Analytical procedures follow EPA Compendium Method TO-11A,[6] with the following deviations:

- Extraction of exposed DNPH sampling cartridges is performed using 3.5 - 5.0 mL of acetonitrile followed by dilution to a final volume of 5 mL with acetonitrile or Type 1 water, well-suited to the HPLC analysis.
- All cartridges (exposed or unexposed) are stored at #4°C except during sampling and shipping. Cartridges are shipped with freezer packs, with a maximum period stored refrigerated/frozen prior to extraction of 30 calendar days. Extracts are analyzed no later than 14 days after extraction.
- The HPLC analysis uses a gradient elution to achieve the desired chromatographic separation of carbonyl compounds, as well as three different mobile phases.
- ERG analyzes each calibration standard three times to determine a calibration curve per EPA Compendium Method TO-11A, using a minimum of six concentration levels. A correlation coefficient of $0.995 for a weighted linear least squares fit of the data is used.
- ERG uses 100 ± 15% as the criterion for recovery for acrolein and crotonaldehyde in the calibration verification standard.
- ERG extracts by flowing solvent in the reverse direction to the air sampling flow.
- The HPLC data acquisition software updates retention time windows using the daily calibration verification standard retention times to compensate for small retention time shifts.

- Stability and reproducibility of the calibration verification standard supports the use of one multipoint calibration curve until the analytical system has changed sufficiently that analysis of the calibration verification sample does not meet acceptance criteria. Multipoint calibration curves are prepared when a calibration verification sample result does not fall within specified acceptance criteria or once every six months at a minimum.

4.8.1.2 Formaldehyde Continuous Monitors

Formaldehyde is a potential carcinogen[49-53] and a prominent compound of atmospheric photochemistry[54]. This gas is one of the products of photochemical oxidation and is significant in motor vehicle exhaust emissions[55,56] and in emissions from combustion processes[57,58]. Scientists who construct mathematical models of the atmosphere in order to predict the effect of different source and sink inventories evaluate these models through diagnostic testing. If the model is correct, it will predict a variation of atmospheric components that compares well with actual measurements. To accomplish diagnostic testing of the model, continuous or semicontinuous (an hour or less) measurements at sub-ppbv and higher concentrations are typical requirements.

Formaldehyde is notoriously difficult to sample and store in part because of its interaction with liquid water and water vapor. Alternatives to storage include reacting formaldehyde with a derivatizing reagent held on a solid substrate, resulting in a product compound which is then stored temporarily and subsequently analyzed. EPA Compendium Method TO-11A[6] is an example of this alternative involving continuous sampling of ambient air through an O_3 scrubber and then through a solid cartridge coated with the derivatizing agent DNPH. The sample is then stored for subsequent separation by HPLC and UV absorbance detection. Although this method has been widely used and has been automated for sequential collection of samples, sample integration times of three hours and usually longer are typical.

One category of semicontinuous monitors also involves derivatization in a multistep reaction referred to as the Hantzsch reaction[59], involving one of the $-diketone compounds and an amine, along with formaldehyde to produce a dihydropyridine derivative. Formaldehyde is

captured from ambient air into liquid water in a diffusion scrubber and then mixed with reagent liquids in a continuously flowing liquid stream. The derivative compound is detected by fluorescence stimulated by a compact light source, e.g., a light-emitting diode. In an EPA-funded research effort, research prototypes have been developed first at Battelle Columbus[60], and later at the Texas Tech University (TTU) Chemistry Department based on their previous research[61]. Cycle time is typically 10 min for the latest TTU prototype and detection limits are sub-ppbv. At least three companies have produced commercial versions based on the Hantzsch reaction. Limited field testing of a TTU research prototype in the summer 1999 Nashville NEO3PS field study and of a commercial version made by AlphaOmega Power Technologies (Albuquerque, NM) in the summer 2001 Philadelphia NEO3PS field study and by EPA, Research Triangle Park, NC, in summer 2002 has occurred with generally good results.[62] Additional field testing by OAQPS/EPA has led to an SOP for the monitor including the description of a procedure to prevent detector problems associated with the formation of air bubbles in liquid transfer lines.[63]

Experience with the commercial unit indicates that weekly replacement of the tubing used in the unit's peristaltic pump and of the liquid reagents held inside the instrument in small plastic reservoirs is required. In addition, waste liquids are generated for proper disposal at longer intervals. Scrubbing chemicals (granular) used for removing formaldehyde from air must also be replaced over time. The zero air for the zero cycle of the instrument is conveniently supplied by using one of the chemical scrubbers.

Instrument calibration for formaldehyde is a critical part of monitoring. Trace formaldehyde in a compressed gas cylinder is available commercially (i.e., 5 parts per million (by volume) (ppmv) HCHO in N_2) so that with further dilution of zero air, a multilevel standard can be dynamically generated. An alternative is to heat trioxane to generate trace formaldehyde[59] for further dilution.

4.8.2 Remote Sensing Applications

Monitoring using several types of remote sensors is potentially applicable to the requirements of the NATTS network. Several of these monitoring systems are presently in use for specialized applications. Factors presently affecting practical application of these types of systems in the NATTS Program are:

- Sensitivity. MDLs for remote sensing systems are typically not consistent with the MDLs achieved with manual technologies currently proposed for use for NATTS;
- Engineering Units. Remote sensing monitoring systems report results as concentration per meter (path integrated) rather than volumetric concentration, as required by NATTS (i.e., : g/m^3 of air sampled);
- Equipment Cost. The purchase price for these monitoring systems is relatively high, as opposed to the moderate cost of most manual sampling systems. However, operational costs may well be less for the remote sensing systems; and
- Complexity. The level of expertise and training currently required for operation of these relatively complex systems in the field is much greater than the expertise and training required to operate a manual collection system.

4.8.2.1 Optical Measurements of Trace Gases for NATTS

UV differential optical absorption spectroscopy (UV-DOAS) measures gases by the absorption of light. An emitter projects a beam of light to a receiver along path lengths typically hundreds of meters. Specific gases absorb light from known parts of the spectrum (i.e., UV visible and IR wavelength ranges). This absorption is recorded using a computer-controlled spectrometer.

With respect to NATTS, UV-DOAS monitoring may be applicable for formaldehyde and benzene. The issues of sensitivity and engineering units, as discussed above, should be addressed to accomplish practical application of this monitoring approach, but if these issues are resolved, the UV-DOAS would provide true continuous monitoring data. The continuous data would

provide many more data points compared to counterpart manual sampling approaches and would allow a better assessment of long-term, temporal, and diurnal trends to be made.

Fourier transform IR (FTIR) spectroscopy as applied to open-path monitoring of atmospheric gases is gradually evolving from monitoring efforts conducted by highly trained individuals experienced in the fields of instrument development and spectroscopy to routine operation of monitoring efforts by trained technicians. EPA Compendium Method TO-16 was written to provide guidance to users for the acquisition of data in a standardized way and to process those data to obtain path-integrated atmospheric gas concentrations. The FTIR can potentially measure the concentration of a large number of atmospheric gases, so the methodology is generalized. (EPA Compendium Method TO-16: Long-Path, Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases (EPA/625/R-96/010b, http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-16r.pdf)

The method is set up in two parts:

- Initial data acquisition after the system has been set up by the manufacturer to produce data that will form the basis of a quality assurance data set; and
- Routine data acquisition to produce time sequences of atmospheric gas concentration data.

In routine monitoring applications as well as during the initial setup, it is required that the ambient temperature and the relative humidity be monitored on a continuous basis so that the water vapor concentration as a function of time can be determined. These data should be acquired at the site where the FTIR data are taken; use of data taken at airports that may be miles away is not adequate.

Trace gas monitoring using FTIR-based, long-path, open-path systems has a number of significant advantages over the traditional methods:

- Integrity of the sample is assured since no sampling actually occurs;

- Multigas analysis is possible with a single field spectrum;
- Path-integrated pollutant concentrations are obtained;
- Spatial survey monitoring of industrial facilities is possible if scanning optics are used;
- Co-adding of spectra to improve detection capabilities is easily performed;
- Rapid temporal scanning of line of sight or multiple lines of sight is possible; and
- Monitoring of otherwise inaccessible areas is possible.

The potential for water vapor interference in FTIR measurement operations can be impacted by the area that is chosen for positioning the FTIR—for example, near large bodies of water when atmospheric conditions may be moisture-laden. Water vapor interference is especially critical when looking at compounds that are within the same absorption band as water.

The ultimate significance of remote sensing with FTIR systems is a matter of cost-effectiveness and of technological advances needed in at least two important areas:

- Improvement in the characteristics of the instrumentation to enhance sensitivity and ease of use; and
- Development of "intelligent" software to improve the means for short-term adjustment of background and water vapor spectra to account for the continual variation of ambient conditions that can adversely affect the accuracy and precision of FTIR-based systems.

It is recommended that on-site meteorological conditions, wind speed and direction, be measured during FTIR measurements.

In addition to EPA Compendium Method TO-16, additional guidance for operation of FTIR ambient air monitoring systems is available in *Open-Path Monitoring Guidance Document*. EPA 600/4-96-040. U.S. Environmental Protection Agency, April 1996; also available at http://www.epa.gov/ttn/amtic/files/ambient/other/lngpath/r-96-040.pdf .

4.8.3 Particle Characterization: Photoacoustic Analyzer

It may be desirable to measure aerosol light absorption by means that do not require the use of filters, and that can observe the aerosol closer to its natural state. The photoacoustic methodology is one way of performing this measurement.[64,65] A photoacoustic analyzer detects and quantifies BC particles in real time, similarly to an aethalometer. A photoacoustic analyzer measures light absorption at a laser wavelength of 1047 nm. BC absorbs very strongly at this wavelength, in contrast to other aerosols and gases. Sample air is pulled continuously through an acoustical waveguide, and the laser also passes through the waveguide. When BC absorbs light, it is heated. This heat transfers very rapidly to the surrounding air in a time that is much shorter than the period of laser-beam modulation, so all of the heat from light absorption comes out of the particles during each acoustic cycle. Upon heating, the surrounding air expands and generates a pressure disturbance (i.e., an acoustical signal) that is measured with a microphone attached to the waveguide. Since BC aerosols absorb light throughout the entire particle volume, the light absorption measurement is also a measure of BC mass concentration. The photoacoustic analyzer measures particles in a flowing airstream without the need to collect the particles on a filter or filter tape, and the photoacoustic analyzer has a very large dynamic range (130 decibels (dB)), making it suitable for a wide range of measurements.

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SECTION 5
DATA MANAGEMENT

5.0 Introduction

After air toxics data have been collected using the required sampling and analytical techniques described in earlier sections, the management of this vast amount of information is key to the success of the NATTS mission. The integrity of the data collected and compiled in an acceptable management system is critical, as they will be used to address human exposure to air toxics. Four areas discussed in this document concerning the data management are:

- data consistency;
- data validation and reporting;
- data archiving; and
- data preparation for entry into EPA's AQS[1] database.

5.1 Data Consistency

Consistency of data is necessary to ensure that the network of sites is collecting data of comparable quality. The network database is only as good as the data it contains, or in other words, "garbage in/garbage out." If bad data are entered, bad information is retrieved, and NATTS calculations may be affected.

Data consistency is the state of understanding the meaning—the semantics—of the data. Although descriptive attributes like data type, length, scale, and domain of values are important, the contextual attributes such as the meaning of each valid value and how and where that value is used in computations and decision making are just as important.[2] Data consistency can be divided into two types of quality: objective quality and subjective quality.

— Objective quality of the data can be achieved fairly easily because the data must meet the specifications required for entry into a data management system (and ultimately AQS). One example is entering units of measure for a sample in ppb when the units of measure from the analytical method are ppm. Another example is date formatting. "010102" may be intended to represent January 2, 2001, but this value may be confused with January 1, 2002. A better way to enter this date, for data consistency, would be "20010102." Systematic internal QC checks from the data management system may identify potential inconsistencies.

— Subjective quality is more difficult to ascertain. An evaluation of subjective quality must consider the mission and goals of the NATTS Program. Data generated should be comparable with other data generated by other sites in the network. To minimize differences in sampling methods, prescribed DQOs must be followed by each NATTS site. The DQOs described in Section 3 are defined as "statements that relate the quality of environmental measurements to the level of uncertainty that decision-makers are willing to accept for results derived from the data." From a subjective quality viewpoint, sites that follow the prescribed DQOs will have higher data consistency than sites that do not.

5.2 Data Validation

"The purpose of data validation is to detect and then verify any data values that may not represent actual air quality conditions at the sampling station."[3] Validation of data is a key component of ensuring data quality. To help ensure data consistency, the techniques for validating data must be the same across all sites in the NATTS Program. In general, the data collected according to a specified methodology are not automatically considered valid. To be validated, the data must be reviewed to confirm that sampling and analysis were performed according to the appropriate method specifications as presented in this TAD and that the execution of these specifications meets the NATTS Program QC requirements. Use of data validation techniques greatly reduces the risk of inconsistent/unacceptable data entering the EPA AQS data management system. Examples of validating field data include checks of monitoring equipment flow rates, sampling times, sample storage conditions, and hold times. If data have potentially been biased by "catastrophic releases" (such as a gasoline spill nearby), those data may be invalidated from the data set as they may artificially affect the data assessment and trend recognition. If a NATTS site is located in close proximity to a chemical manufacturing plant and a benzene leak occurs at

the plant on a sampling day, the sample may show a very high ambient concentration of benzene. The resulting monitoring data should be flagged for later evaluation during the review process. The site logbook should also be reviewed for any unusual circumstances recorded during a sample collection period.

Laboratory data must be validated to confirm that the QC requirements for blanks, calibration curves, and regular calibration checks meet the method requirements as presented in this TAD. A simple data validation technique may involve as little effort as comparing the measured value of a NATTS Program target compound with its MDL. For example, if a NATTS Program site measures a formaldehyde concentration of 0.025 ppbv using EPA Compendium Method TO-11A, but the associated MDL for the sampled volume is 0.051 ppbv, the measured value is less than the method MDL. However, **for the NATTS Program, the "measured" data must be reported and appropriately flagged as being below the MDL**. Review of data should also confirm that any concentration of a target compound is not above the upper limit of the calibration curve for the method.

The objectives for data validation should include the following:

- To produce a database with values that are validated and of known quality;
- To evaluate the internal, spatial, temporal, and physical consistency of the data; and
- To intercompare data to identify errors, biases, or outliers.

A typical sequence of events for data validation includes the following steps:

- As soon as samples are received at the laboratory from the field, the COC documentation is checked to verify the sample identity and to invalidate samples with sampling anomalies;
- After sample analysis, a reviewer verifies that all samples were prepared and analyzed within method-specified hold times;

- The analyst preparing the sample verifies that all samples are prepared following individual method specifications;
- The instrumental analyst reviews the compound ID information obtained by the analytical instrumentation (GC/MS, HPLC, IC, ICP/MS);
- A second reviewer verifies the analyst's determinations and prepares a report;
- The peer reviewer reviews the quarterly report for a sample set, from sampling to analytical detection and quantitative analysis and final report; and
- The peer reviewer prepares a statistical spreadsheet for all samples per site per year to verify the sample group by calculating and reviewing the frequency of detects; low, high, and median detection; arithmetic and geometric mean; SD; and CV for each compound.

Data validation should include the use of statistical analysis to determine invalid data. All statistical terms used in this section can be found in *Introduction to Probability and Statistics*[4]. As data are collected over a period of time, the statistics derived below can be compared against the historical data set. Preparation of a scatterplot and/or boxplot of NATTS Program site data is an effective way to visually determine potential outliers from the main body of data. Potential outlier data should be rigorously reviewed to determine whether contamination or operational errors occurred, which would invalidate the data. Data that have been submitted to AQS have been shown to still contain calibration data, data influenced by operational problems, species misidentification, and contamination problems.

Another statistical procedure for data evaluation includes determining the central tendency of the data set. There are four different ways to describe this central tendency:

- Arithmetic mean. The sum of the measured concentrations divided by the number of samples;
- Geometric mean. The result of multiplying the concentrations of samples with each other and taking the n^{th} root of the number (n) of samples (e.g., for a data set with 20 concentrations, the 20^{th} root of the product would be taken);

- Median. The concentration value that represents the midpoint of the data set when arranged in order of magnitude (e.g., 50% of the data is greater than the median and 50% of the data is less than the median); and

- Mode. The concentration that has the highest frequency.

Data analysts calculate these values to identify outliers for data validation. It is very important to proceed from the "big picture" to a closer view, proceeding from a month of data to a week and then to a day. This strategy is important in forming an overall understanding of the data. Another important factor is to inspect every species that is reported, even when low concentrations are expected. Data validation is critical because serious errors in data analysis, modeling results, and trends analysis can be caused by erroneous individual data values. Sonoma Technology, Inc. (STI), has developed VOC data validation and analysis software named VOCDat.[5] STI provides this software at no cost to local, state, and regional agencies throughout the United States for use in preparing their VOC data for submittal to the U.S. EPA's data repository, AQS. VOCDat enables an analyst to screen VOC data for outliers and display data using time series, scatter, and fingerprint plots. [VOCDat software and its user guide can be downloaded free from ftp://ftp.sonomatech.com/public/vocdat/ .] VOCDat also displays other air quality parameters such as toxic compounds, O_3, NO_x, and meteorological measurements. The three types of plots useful in data evaluation are discussed in more detail below.

— Time series plots. To take full advantage of time series plots, the time series of every species and species group should be plotted and inspected to identify outliers, calibration spikes, abrupt changes in concentrations, possible misidentification of peaks, and extended periods of unusually high or low concentrations. It is useful to plot species together which are primarily emitted by the same type of source (e.g., benzene and acetylene are both present in automobile exhaust), or to plot species together which are emitted from different sources. A time series plot, as shown in Figure 5.2-1, can be useful in the investigation of diurnal behavior of pollutants.

— Scatter plots. In preparing scatter plots, several pairs of species or species groups such as benzene and toluene, benzene and acetylene, benzene and ethane, and other pairs should be plotted and inspected. Scatter plots, as shown in Figure 5.2-2, are useful for comparing the relationship between species at one site or at a pair of sites.

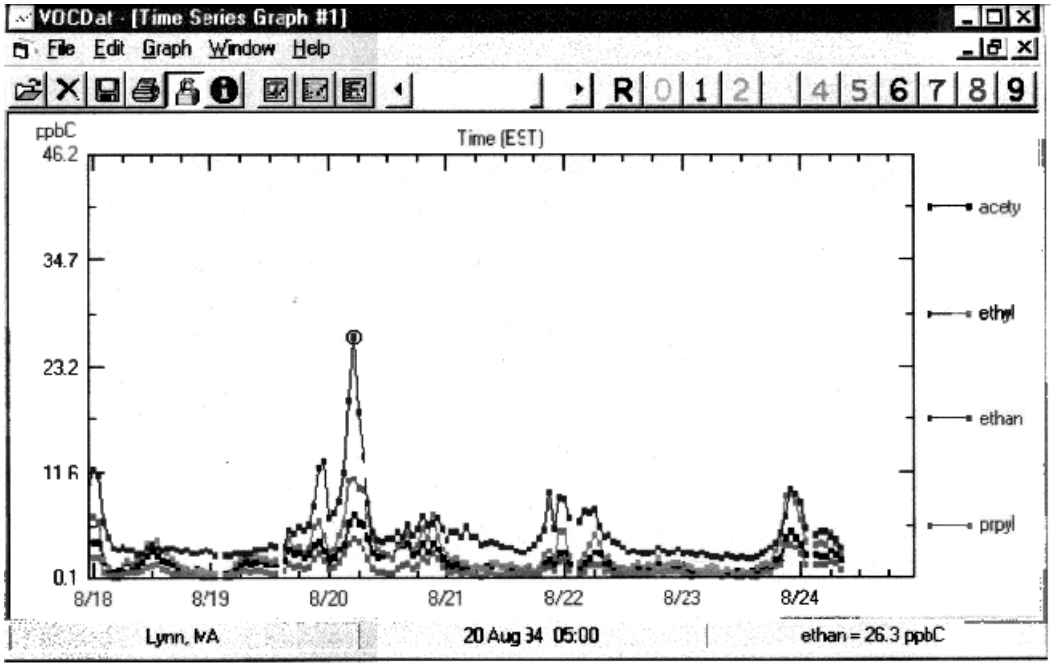

Figure 5.2-1. A Time Series Plot Illustrating Acetylene, Ethylene, Ethane, and Propylene

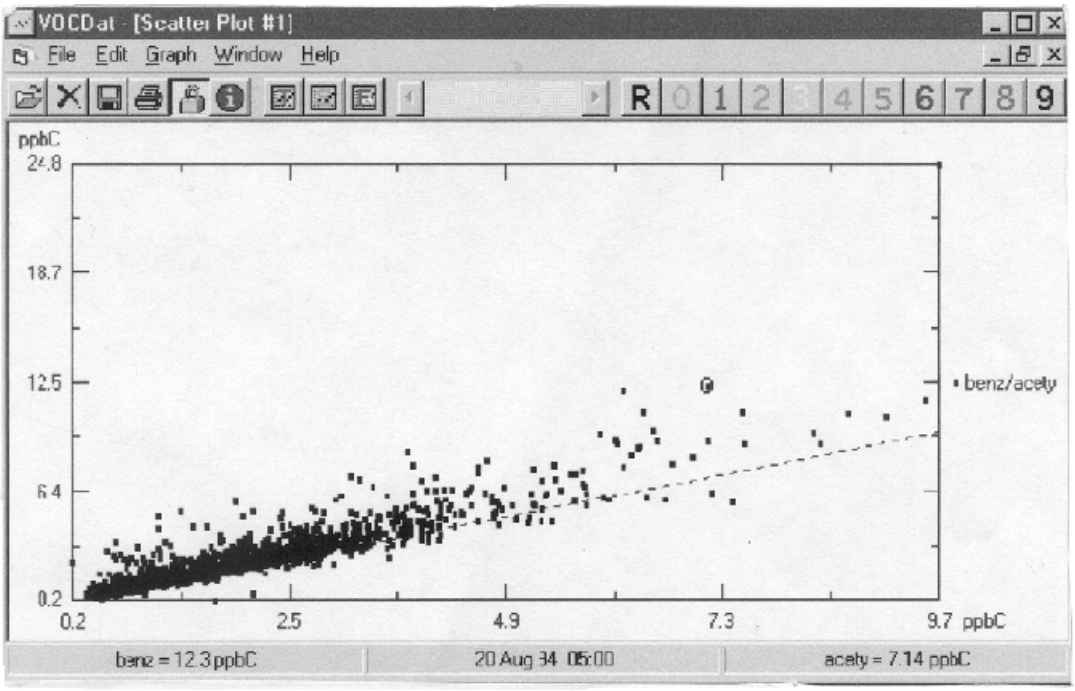

Figure 5.2-2. A Scatter Plot Illustrating the Relationship between Benzene and Acetylene at a Site

— Fingerprint plots. Fingerprint plots show the concentration of each species in a sample (in chromatographic order) and help to identify unique characteristics of the samples. Fingerprint plots should be inspected quickly and fingerprints of samples that have been flagged (i.e., identified as suspect or invalid) should be inspected in time series or scatter plot analyses. Checking fingerprint plots one-by-one allows an analyst to observe diurnal changes in species or species groups quickly. The analyst should then inspect hours or days surrounding suspect and invalid data to see if there is any carryover effect. A fingerprint plot for toluene at a monitoring site is shown in Figure 5.2-3.

Final data validation will be performed by EPA in the process of calculating trends in NATTS compounds concentrations. For each NATTS Program site, more sophisticated data validation techniques include calculating the following statistical parameters for a data set:

— The variance (or dispersion). The average of the square of the deviations of the measurements about their mean;

— The standard deviation. Equal to the positive square root of the variance; and

— The confidence interval. Uses the SD and size of the sample population, along with a t-value, to determine the statistical range in which the arithmetic mean may reside under a *normal* distribution.

Individual confidence intervals and coefficients of variation will be compared to the DQO coefficient of variation (i.e., ± 15%) as final validation for use of the data in trends analysis.

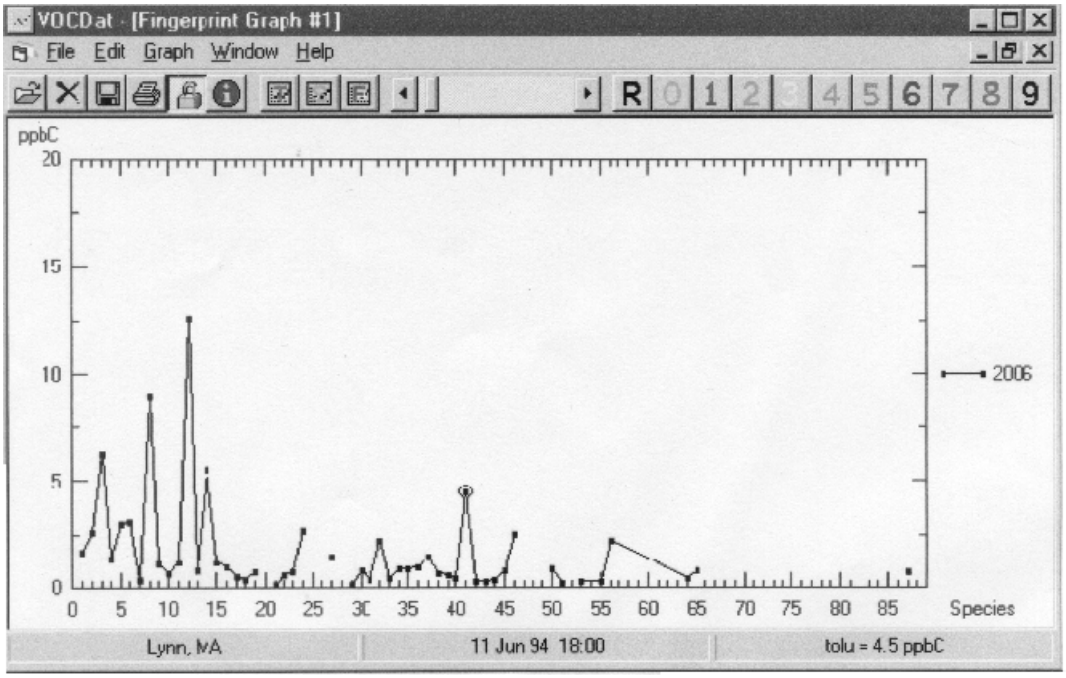

Figure 5.2-3. A Fingerprint Plot Illustrating the Changing Concentration of Toluene Over Time at Hourly Intervals

Data reporting provides a regular summary of the results and observations made during NATTS Program monitoring. Standardized electronic and hard copy reports of validated data must be provided quarterly to the EPA NATTS Program management team for review. The data must also be submitted to EPA's AQS database quarterly.

5.3 Data Archiving

Data archiving is the backing up and storage of data that must be retained but not regularly accessed.[6] After data have been validated, all the data must be archived in a manner that is easily accessible and retrievable. Data should be archived on a permanent electronic medium (i.e., CD-ROM). An electronic copy and a hard copy of the data should be stored for a period of no less than six years in a separate physical location from the laboratory or field site to minimize the potential for data loss.

5.4 Data Entry into AQS

EPA's AQS[1] contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from thousands of monitoring stations. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data QA/QC information. AQS users rely upon the system data to assess air quality, assist in attainment/nonattainment designations, perform modeling for permit review analysis, and other air quality management functions. With quarterly reporting of data to AQS, the NATTS Program will use data gathered in AQS to assess trends in air quality data. AQS information is also used to prepare reports for Congress as mandated by the CAA.

The AQS database is EPA's data management repository for NATTS Program network data, which contains validated measurements of ambient concentrations of air pollutants and associated meteorological data. As with other types of EPA ambient air monitoring programs (i.e., criteria pollutants, PAMS, etc.), NATTS Program data must be prepared and entered into AQS. Data preparation and entry is the responsibility of each participating agency. AQS features a graphical interface but now requires a new and different coding for entry of data. The new code is more flexible and allows a greater volume of event-specific information to be entered into the database. Some fields are no longer restricted to a certain number of characters, and currently each field is separated by a pipe delimiter (*).

Data entry into AQS presents a certain amount of challenge, especially to the inexperienced user of the database. The first step in uploading data to AQS is to ensure a successful connection to the AQS Oracle® database and Unix® servers. Due to security upgrades, establishing a connection to the EPA servers can prove to be complicated and difficult. Screening group access is required for entry of data into the AQS. Specific information and assistance can be obtained by contacting AQS technical support (at 800-334-2405). The manuals and guides indicated in Table 5.2-1 are available for AQS.

Table 5.2-1. Manuals and Guides Available for EPA's AQS

Manual (Date)	File Name	File Type
AQS Data Coding Manual (3/25/03)	AQS Data Coding Manual, v1.3.pdf	Adobe Acrobat
	Clarification of numeric field lengths in data coding manual	Adobe Acrobat
AQS Data Dictionary (3/26/03)	AQS Data Dictionary, v1.1.pdf	Adobe Acrobat
Appendices for Data Coding Manual and Data Dictionary (5/9/02)	Data Coding and Dictionary Appendices.pdf	Adobe Acrobat
Guide	**File Name**	**File Type**
Input Transaction Formats (9/4/02)	aqstrans_format.pdf	Adobe Acrobat
Quick Look Work File Formats (5/31/02)	QuickLookWorkfileFmts.pdf	Adobe Acrobat
AQS User Guide Covers Installation, Accounts, Data Input, Maintenance, and Data Retrievals (4/19/02)	AQSUserGuide_v1.doc	MS Word 2000
Selected AQS Code Descriptions	Selected AQS Code Descriptions	HTML
Acronyms and Abbreviations (2/27/03)	Acronyms & Abbreviations	Adobe Acrobat
Online Training modules (6/26/02)	online_training_modules_V2-2.EXE	self-extracting download
PARSV2 User Guide (11/20/02)	PARS User Guide with Appendix	self-extracting to Adobe Acrobat (pdf)
Material	**File Name**	**File Type**
Training Modules (3/14/02)	classroom_training.zip	zipped
Class Handouts (3/14/02)	handouts.zip	zipped
Class Exercises (3/14/02)	exercises.zip	zipped
Quick Reference (4/19/02)	AQS Quick Ref V4.pdf	Adobe Acrobat

5.4.1 VOCDat

VOCDat is a software package developed to display VOC data, to perform QC tasks on the data, to allow an analyst to begin exploratory data analysis, and to prepare data for entry into EPA's AQS database. VOCDat can be used for data collected on an hourly basis with automated gas chromatography systems or on other sampling intervals (e.g., 3-hour, 24-hour) with canisters. One of the goals underlying the development of this software was to enable states to rapidly validate and release their data. The software itself, with a manual[5] that provides a description of the software, tells how to use the software, and gets technical or operational questions answered free by the developers of the software (STI) at ftp://ftp.sonomatech.com/public/vocdat/ .

VOCDat software was designed for the display, QC, and analysis of VOC data. Concentrations of target species may be displayed using scatter plots, fingerprint plots, and time series plots, to compare samples at a single site or at different sites. QC codes may be changed for individual or selected groups of data points as well as for the entire sample on all plots. Customizable screening criteria can be applied to the data to assist the user in identifying possible problems.

VOCDat will also calculate the weight percents of the data or multiply the concentration or weight percents by reactivity factors.[7] The resulting altered data sets can then be explored using the graphical features of the VOCDat software. VOCDat calculates species groups, including total unidentified hydrocarbons, sum of the target species, total aromatic hydrocarbons, total olefins, total paraffins, and total carbonyl compounds. In addition, other air quality and meteorological data (such as O_3, NO_x, wind direction, etc.) can be added to the VOC database, and new calculated data fields may be created (such as ratios between various parameters). Finally, the air toxics and carbonyl concentration data can be exported in a format suitable for submittal to the EPA AQS data system or in a format easily importable into spreadsheet or statistical software packages.

Three screening tests for data are currently available in VOCDat: checks of the abundant species concentrations, comparison of concentrations, and variability in concentrations. A module

for the computation of summary statistics is also available. Most VOCDat screens and statistics can be applied to the concentration, weight percent, or reactivity factor-weighted data.

At most ambient air monitoring sites across the United States, there is a common set of hydrocarbon species that are typically abundant including acetylene, ethane, propane, *n*-butane, *i*-pentane, *n*-pentane, *n*-hexane, benzene, toluene, and the xylenes. Experience shows that if most of these species are present at relatively high concentrations (above 1 ppbC), all of these species should probably be present above the detection limit. VOCDat provides a means of testing for these compounds that should be present at relatively abundant concentrations. The program provides default criteria, but as more experience is gained with a specific monitoring site, the criteria can be customized to better represent the site under investigation. Screening concentrations should be set low enough to limit the number of failures for the screening criteria but high enough to be meaningful (say, 10 times the detection limit). The species list should reflect the most abundant species (or, perhaps, the most problematic species) at the site and should therefore be customized by the user.

In addition to commonly present hydrocarbons, there are also relationships among VOCs that are apparent at many sites. VOCDat provides a check of several expected relationships. For example, all three xylene isomers (*ortho-, meta-, and para-*) tend to be present at about equal concentrations at ambient sites in and near urban areas. Since the *m*- and *p*-xylenes typically coelute in most gas chromatographic systems and have identical mass spectra, the concentration of the sum of these two species should exceed the concentration of *o*-xylene. Thus, one check of the data could be to see whether *o*-xylene concentrations are greater than the sum of the *m*- and *p*-xylenes. This concentration comparison will bring this data set to the attention of reviewers, who can resolve the question of whether the particular site has a source of *o*-xylene independent of the other two isomers. In addition to a one-on-one check of species concentrations, the user of VOCDat can also check for species concentrations above a cutoff value or above a certain weight percent. When screening criteria are applied, VOCDat checks each sample record for data that do not fit the specified criteria. As with the other criteria, users can start with default criteria, and as

more experience with their own data is gained, the criteria can be customized to better represent the site.

Another set of quality checks on the data includes a check of the sample concentrations that lie outside the majority of the sample population. It is also useful to determine a list of outliers using simple statistics in order to provide a check on the data independent of the graphical checks on the data. For a concentration variability check, the abundant species or species group concentrations can be compared to the overall sample population using the SD. As with other criteria, users of VOCDat can start with default criteria, and as more experience with their own data is gained, the criteria can be customized to better represent the site.

Summary statistics of a data set, including the minimum, maximum, median, mean, and SD, are useful for assessing the variability in the data. VOCDat files can be imported to other software packages for the computation of these values, or these values can be calculated through VOCDat.

Data entered into VOCDat are exported directly into AQS. One of the functions VOCDat serves is to provide a uniform approach to generating the code required to enter validated data into EPA's AQS for NATTS data. Once data have been successfully imported into VOCDat, a user can export the data into a text file. VOCDat offers one approach to generating the code required to enter validated data into AQS; other approaches are available, as indicated above.

5.4.2 EPA's AQS—Input of Data Related to Airborne Pollutants

EPA's AQS is a computer-based system for handling storage and retrieval of information pertaining to airborne pollutants. AQS is administered by the EPA, OAQPS, in Research Triangle Park, NC. AQS contains data from state and local agencies, tribes, and federal organizations, including descriptions of air monitoring sites and monitoring equipment, measured concentrations of air pollutants and related parameters, and calculated summary and statistical information. Reporting agencies submit air quality data as formatted transactions using File Transfer Protocol (FTP).

Nineteen types of transactions are used to provide data and control information for updating the AQS database, with detailed instructions available for coding individual transactions.[8] Four general types of values are used to code air quality transactions: codes, dates, numeric data, and alphanumeric data. Each of these values must be entered on transactions exactly as they are stored in the AQS tables. The 19 AQS transaction formats contain certain fields in common, as well as unique fields:

- The transaction type specifies which batch transaction is being processed by the batch load software and determines which tables and columns will be updated with the data in the delimited fields;
- The action code indicates the data manipulation action to be performed by the transaction;
- The state code identifies one of the 50 states, U.S. territories, Washington, DC, or foreign countries;
- The county code identifies a county or equivalent geopolitical entity such as parish or independent city. For foreign countries, the county code identifies the geopolitical equivalent to U.S. states, such as Mexican states or Canadian provinces;
- The site ID is a numeric code that uniquely identifies each air monitoring site within a county. Site numbers are not assigned continuously or in any particular order. Local organizations are free to allocate site numbers in any way they choose as long as there is no duplication within a county;
- A set of three site transactions is used to update site information:
  - Type AA (Basic Site Information)
  - Type AB (Site Street Information)
  - Type AC (Site Open Path Information).
- A set of 11 transactions is used to update monitor information in the site file:
  - Type MA (Basic Monitor Information)
  - Type MB (Monitor Sampling Periods)
  - Type MC (Monitor Type Information)
  - Type MD (Monitor Agency Role)
  - Type ME (Monitoring Objective Information)
  - Type MF (Monitor Sampling Schedule)
  - Type MG (Monitor Street Description)
  - Type MH (Monitor Obstruction Information)

  - Type MI (Monitor Regulatory Compliance)
  - Type MJ (Monitor Collocation Period)
  - Type MK (Monitor Protocol).

- Raw Data Transactions
  - Type RC (Composite Raw Data)
  - Type RD (Hourly, Daily, and Subhourly Raw Data).

- Accuracy/Precision Transactions
  - Type RA (Accuracy Data)
  - Type RP (Precision Data)

- Annual Summary Data (Transaction Type RS).

AQS codes for air toxics are summarized in Appendix A.

This is where whatever edited version we use of the Summary Table of codes will go.

5.4.3 VOCDat® and AQS

Perhaps the most common data format used to import data into VOCDat® is an AQS format file such as that which is submitted to or retrieved from the EPA AQS database using the card image file format (e.g., 80 characters per line). VOCDat® can export data in the AQS R-2 format suitable for submittal to EPA's AQS database. Data with a QC code of 8 (invalid) are not exported to AQS. Data with QC codes of 1 through 6 are exported as null codes rather than concentrations (null codes for AQS are letters and letter combinations rather than numbers). Samples that have been flagged as suspect (QC code = 7) are exported to AQS with no annotation. Only concentration data for each species are exportable in R-2 format; R-2 format files for AQS cannot be created with retention time, MIR-scaled, or weight percent data.

In VOCDat®, AQS format files are given an *.AIR extension (e.g., filename.air). To export to the AQS format, open a *.VOC file and choose "File – Export – new AIRS." The user receives information dialog that includes input for state, county, and site codes; POC code; method code; and action code. The option to fill time gaps in the data is provided along with a null code (letters

and letter combinations) for the gaps. The user can specify which species to include in the export. For reference, the minimum and maximum values for each species are provided in the information dialog window. Buttons to aid in selecting species for export are provided:

- In Use = selects species that are present in the current file.
- All = selects all species listed in the species.txt file.
- Clear = clears all check marks so that the user can start over.

After providing the information for the information dialog screen, the user clicks “OK”. VOCDat® then creates an *.AIR file that contains concentration (in ppbC and/or ppmC if necessary) or an AQS null code for each species.

Section 5: References and Resources

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Appendix A

Draft Report on Development of Data Quality Objectives (DQOs) for the National Ambient Air Toxics Trends Monitoring Network

The following draft report was produced through collaboration with the Toxics Workgroup whose goal was to develop data quality objectives for the National Ambient Air Toxics Tends Network. This report was written by Battelle Laboratories who facilitated Workgroup discussions and provided statistical assistance in developing the simulation models and performance curves.

1.0 INTRODUCTION

The Data Quality Objective (DQO) process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected by EPA meets the needs of the intended decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet a program's goals. The DQO process was applied to one of the primary goals of the National Air Toxics Monitoring Network, namely:

> ***To be able to detect a 15% difference (trend) between two successive 3 -year annual mean concentrations within acceptable levels of decision error.***

Being able to detect this trend would allow one to evaluate the effectiveness of HAP reductions. This report documents the results of the DQO process for the local monitoring data requirements for: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde.

The technical approach used followed the conceptual model developed for the $PM_{2.5}$ FRM DQOs. This conceptual model was followed mainly due to its success in use with $PM_{2.5}$ and the flexibility of the conceptual model. It is a quite general model for simulating the characterization of ambient concentrations in terms of annual or multi-year averages from 1 in n day sampling. The model incorporates several sources of variability: seasonal variability, natural day-to-day variability, sampling incompleteness, and measurement error. The measurement error was restricted to a precision component without a bias component because the final mathematical form of the assessment of trends is robust to multiplicative bias. Pollutant specific parameters were used in the modeling. The parameters describing the natural variation of the pollutants were based on data analyses of the Pilot City data and the Air Toxics Archive. Finally, separate urban and rural DQOs were established for the pollutants that were sufficiently measured in rural locations of the Pilot Study.

A workgroup organized by EPA/OAQPS/EMAD provided representatives of data users, decision makers, state and local parties, and monitoring and laboratory personnel. Battelle provided technical statistical support throughout the process with examples and data analyses. The workgroup guided the DQO development and made the decisions that were not driven by data analyses in the DQO development during a series of conference calls. These decisions included items such as establishing a specific mathematical form for measuring trends and establishing limits on the sampling rate. Battelle and EPA also held a meeting in Research Triangle Park, North Carolina, on June 17, 2002 to discuss the development details.

2.0 THE GENERAL DQO PROCESS

This section presents an overview of the seven steps in EPA's QA/G-4 DQO process as applied to one of the primary goals of the National Air Toxics Monitoring Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies (see

www.epa.gov/quality/qa_docs.html). The purpose of this section is to provide general discussion on the specific issues that were used in developing the DQOs as they relate to the general DQO process.

The DQO process is a seven-step process based on the scientific method to ensure that the data collected by EPA meet the needs of its data users and decision makers in terms of the information to be collected, in particular the desired quality and quantity of data. It also provides a framework for checking and evaluating the program goals to make sure they are feasible and that the data are collected efficiently. The seven steps are usually labeled as:

- State the Problem
- Identify the Decision
- Identify the Inputs to the Decision
- Define the Study Boundaries
- Develop a Decision Rule
- Specify Tolerable Limits on the Decision Errors
- Optimize the Design.

This section has general discussion for each of these items. The pollutant specific outcomes of the DQO process are contained in Section 3.

2.1 State the Problem

Characterize the ambient concentrations in the region represented by the monitor to establish any significant downward trend (measured by a percent change between successive 3-year means of the concentrations).

The ability to characterize the trends was statistically modeled. The statistical model was designed by starting with a model similar to the one used for $PM_{2.5}$ FRM data. The ambient concentrations are modeled as deviations from a sine curve, where the sine curve represents seasonality. This sine curve represents long-term daily averages of the concentrations that one would observe at the site. The form used is as follows:

$$A\left[1+\left(\frac{r-1}{r+1}\right)\sin\left(\frac{day}{365}2\ p\right)\right]$$

where

A = the long term annual average and
r = the ratio of the highest point on the sine curve to the lowest point. A value of r = 1 indicates no seasonality.)

The natural deviations from the sine curve are assumed to follow a lognormal distribution with a mean that is given by the particular point on the sine curve. (For example, the value of the sine curve for Day 100 is the mean for all Day 100s across many years.) The coefficient of variation (CV) of the lognormal distribution is assumed to be a constant. The general model considered also allows for the day-to-day deviations from the sine curve to be correlated, but the current DQOs are based on a correlation of zero. The correlation effectively measures how quickly the concentrations can change from one deviation from the sine curve to another. A correlation of zero indicates that it can change fast enough that values measured on consecutive days would be completely independent. A value of 0.2 would say that a positive deviation from the curve is somewhat more likely to be followed by another positive deviation than a negative deviation. A value of 0.9 would indicate that positive deviations are almost always followed by another positive deviation. Finally, the measured values are modeled with a normally distributed random measurement error with a constant coefficient of variation (CV). The specific values for the various parameters are pollutant specific.

The population parameters (the degree of seasonality, the autocorrelation, and the CV of the deviations from the sine curve) were estimated from the Pilot City data (and in the case of benzene compared with estimates from the Air Toxics Data Archive). (See Attachment 1.) A near worst-case choice was made for each of the parameters. The power curves and decision errors are established via Monte-Carlo simulation of the model with the particular parameters for various combinations of truth and observed percent changes in three-year mean concentrations. The power curves are plotted as functions of the true percent change in the three-year annual means for compound specific combinations of the sampling frequency, completeness, and precision. Decision errors are stated for these worst-case scenarios.

Note: It was decided by the workgroup from budgetary considerations that the proposed DQOs should be constrained to no more than one in six day sampling.

2.2 Identify the Decision

The decision statement should provide a link between the principal study question and possible actions. The potential actions associated with achieving or failing to achieve a particular percent decrease in the observed three-year mean concentration were not defined by the workgroup. However, it was decided that any decision would be based on whether or not a 15 percent decrease was observed. Hence the form of the decision was fixed, and may be specified as follows:

> *Significant decreases (15 percent or more) between successive three-year mean concentration levels will result in … Insignificant decreases, (increases, or decreases of less than 15 percent) will trigger alternate actions of .*

2.3 Identify the Inputs to the Decision

Only six HAPs (benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde) were considered in the DQO development. It is assumed that the other pollutants will be represented by at least one of these six. The statements included here apply implicitly to the other HAPs.

It is assumed that the analytical techniques used in the Pilot study will be used throughout the program. Most importantly for the DQOs the Method Detection Limits (MDLs) will not increase. The pollutant specific MDLs assumed are listed in Section 3. Those values were identified as pollutant-site maximums that were achieved by at least two of the pilot sites in each pollutant's case.

Among the key decisions made as a part of the DQO process was that each pollutant will need to be measured on a schedule of at least once every six days with a quarterly completeness of 85 percent for six consecutive years. The completeness criterion was checked against the pilot data, and was generally achieved. All valid measurements count toward the completeness goal, including non-detects. The analysis of the trends at the site level will be based on a percent difference between the mean of the first three annual concentrations and the mean of the last three annual concentrations. Hence for each year the annual average concentration, X_i, needs to be found, i = 1, 2, … 6. Next find the mean, X, for the first three years and the mean, Y, for years 4 through 6 as follows:

$$X = \frac{X_1 + X_2 + X_3}{3} \text{ and } Y = \frac{X_4 + X_5 + X_6}{3}.$$

Then the downward trend, T, is the percent decrease from the first three-year period to the second three-year period. Namely,

$$T = \frac{X - Y}{X} \cdot 100 .$$

The Action Level is the cutoff point that separates different decision alternatives. Based on the assumed budgetary constraint of one in six day sampling and the natural variation exhibited by the six compounds considered, an action level of 15 percent was chosen. Hence at least a 15 percent decrease between the two distinct three-year mean concentrations will need to be observed in order to be considered a significant decrease. This assumes that the mean concentrations are above the health standards, and hence it makes sense to consider trends. (Note that characterizing the mean concentrations is a separate goal of the Air Toxics program that has not yet been considered and could result in different DQOs.)

2.4 Define the Study Boundaries

It is desired that the specific location of the monitors be constrained so that they represent neighborhood scale assessment for each of the two three-year periods under consideration. The

details of how to ensure this goal have not yet been determined. Some guideline is provided by the Air Toxics Monitoring Concept Paper (see http://www.epa.gov/ttn/antic/airtxfil.html).

2.5 Develop a Decision Rule

The decision rule is an "if ... then" statement for how the various alternatives will be chosen. As noted above the specific alternative actions have not been formalized yet, just the form of the decision rule.

> *If the percent change between successive three-year average concentration levels is greater than or equal to 15 percent, then …Otherwise …*

2.6 Specify Tolerable Limits on the Decision Errors

Since the program will not generate complete, error-free data, there will be some probability of making a decision error. The main goal of the DQO process is to find a workable balance between how complete and error free the data are with acceptable levels of decision errors. To find the balance, the possible errors need to be carefully defined. This usually needs to be done with the recognition that there will be a range, often called the gray zone, where it is impractical to control decision errors.

The QA/G-4 guidance recommends using 0.01 as the starting point for setting decision error rates. However, such a limit would generally require a sampling rate that is not feasible. The workgroup decided on the following limits:

> *If there is no true decrease in the three-year average concentrations, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.*
>
> *If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is less than 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.*
>
> *Equivalently, the second statement could read that:*
>
> *If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be at least 90 percent.*

The power curves shown in Section 3 show the probability of observing at least a 15 percent decrease as a function of the true decrease. In terms of the above goals this means that the power curve graphs should start below 10 percent for a true percent

change of 0 and end above 90 percent for a true percent change of 30 percent. Since there is a particular interest in the error rates for no true change and for a true change of a 30 percent decrease, this associated x-axis (horizontal axis) range is shown for each curve. Also, it is sometimes useful to know when the two target error rates are achieved. The range of "truth" between these values is referred to as the gray zone, i.e., the range of true percent decreases that cannot be reliably detected by the sampling scheme. These are also given for each curve (and indicated with vertical dotted lines).

2.7 Optimize the Design

In each pollutant's case, a sampling schedule of once every six days is set forth with a quarterly completeness criteria of 85 percent. Pilot City study participants were surveyed and almost all were collecting and obtaining valid data values at a rate that exceeded 85 percent for each of the six compounds considered (valid non-detects counted toward completeness). Hence, the target rate of 85 percent was selected, instead of the more common 75 percent completeness goal. This should make the power curves more representative of the network's expected monitoring conditions.

3.0 DQOS FOR THE SIX STUDY COMPOUNDS

This section states the design values, namely it gives the expected maximum error rates, gray zones, and power curves for each of the six compounds considered explicitly. The parameters describing the natural state of the ambient conditions used to construct the power curves, error rates and gray zone are compound specific based on data from the Pilot Study. (See Appendix A.) In each case, the Pilot City data yielded a range of estimates. The specific values used were the extremes (or nearly so) that would make detecting a downward trend more difficult. Actual performance in almost all cases should be better than that indicated by the power curves, since specific sites would not be characterized by these extremes in each of these parameters. However, since the sensitivity to the different parameters is not the same, the DQOs need to protect against a combined set of extremes. Hence, the use of extremes for network design purposes is conservative.

Since the rural sites can be quite different from urban sites, separate DQOs are shown in those cases where there were sufficient data to support investigating a separate set of DQOs. In the case of formaldehyde, the urban and rural DQOs are essentially the same.

There are twelve input parameters shown in each section. They are:

1. T1. This is the target error rate for when there is no change. It is always 10 percent.

2. T2. This is the target error rate for when there is a 30 percent decrease. It is always 10 percent.

3. The action limit. This is the minimum observed percent change from the mean concentration of the first three years to the mean concentration from the last three years that would be used to indicate that the concentrations have decreased.

Decreases less than this amount would not be considered significant decreases in the mean concentration.

4. The sampling rate. It is set to one in six day sampling in each case.

5. The quarterly completeness criterion. This was set to 85 percent based on the recommendation of ERG and a review of the Pilot Study data completeness.

6. Measurement error Coefficient of Variation (CV). This was assumed to be 15 percent for each compound. (A sensitivity analysis showed that the DQOs are robust to moderate changes in this value.)

7. Seasonality ratio. This is a measure of the degree of seasonality. Specifically, it is the ratio of the highest point on the seasonal curve to the lowest point. A value of 1 indicates no seasonality. Larger values make it more difficult to estimate an annual or three-year mean concentration, and hence larger values make it more difficult to measure the percent change.

8. Autocorrelation. This is a measurement of how quickly day-to-day deviation from the seasonal curve can occur. A value of 0 indicates that changes occur quickly enough that each day is independent of the preceding day. Values greater than 0 indicate that the changes are generally slower, so that days with concentrations above the seasonal curve are more likely to be followed by another day above the seasonal curve. Values greater than 0 increase the precision of the three-year means and the percent change between the three-year means. Hence, a value of 0 is the most conservative choice for the DQOs. Zero was used in all cases, because many daily measurements are required to obtain a reliable estimate of this parameter.

9. Population CV. This is a measurement of the natural variation about the seasonal curve. Larger values decrease the precision of the three-year mean concentration estimates and the percent change between them. The power curves are strongly dependent on this parameter, but the estimates can be strongly influenced by a few outlier values. Generally the 90^{th} percentile of the estimates from the Pilot study was used as a balance between these competing forces. This value was then rounded up to be a multiple of 5 percent for the urban DQOs. For the rural DQOs an additional 5 percent was added, since there were fewer rural sites on which to base the estimates.

10. MDL. This is the MDL used in the simulations. The value was chosen to be a reasonably attainable maximum for a site and compound.

11. Initial mean concentration. This is the mean concentration of the first three years in the simulations. Values closer to the MDL decrease the precision of the percent change estimate. The value chosen was approximately equal to the 25^{th} percentile of the site-compound means from the Pilot study.

12. Health Risk Standard. This value is shown for reference only. It was not used in the simulations.

In addition to the power curves, there are three sets of output values.

1. $Error_0$ is the percent of the simulations with no change in the true three-year means that in fact generated at least a 15 percent decrease in the observed three-year means. The goal is $\leq$ 10%

2. $Error_{30}$ is the percent of the simulations with a 30 percent decrease in the true three-year means that generated less than a 15 percent decrease in the observed three-year means. The goal is $\leq$ 10%

3. The gray zone is the interval of the true decreases that cannot be detected with confidence by the study design. In this range, the probability of observing at least a 15 percent decrease is greater than 10 percent, but less than 90 percent.

In summary, based on variability and uncertainty estimates from the ten-city Pilot Study, the following Sections 3.1 through 3.10 suggest that the specified air toxics trends DQOs will be met for monitoring sites that satisfy the goals of 1 in 6 day sampling, 85 percent completeness, and 15 percent measurement CV. These results were explicitly developed for benzene (urban and rural); 1,3-butadiene (urban and rural); arsenic (urban and rural); chromium (urban only); acrolein (urban only); and formaldehyde (urban and rural).

3.1 DQOs for Measuring the Percent Decrease of Benzene at Urban Locations

Table 3.1.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at urban locations. Table 3.1.2 shows the output values from the simulations. Figure 3.1.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.1.2 suggests that the specified air toxics trends DQOs will be met for benzene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.1.1 DQO input parameters for benzene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.5	85%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.044	0.128

Table 3.1.2 DQO output parameters for benzene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
6%	3%	3% - 26%

Figure 3.1.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in urban locations of the Pilot Study

3.2 DQOs for Measuring the Percent Decrease of Benzene at Rural Locations

Table 3.2.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at rural locations. Table 3.2.2 shows the output values from the simulations. Figure 3.2.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.2.2 suggests that the specified air toxics trends DQOs will be met for benzene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.2.1 DQO input parameters for benzene at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	4.0	60%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.044	0.128

Table 3.2.2 DQO output parameters for benzene at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
2%	1%	7% - 23%

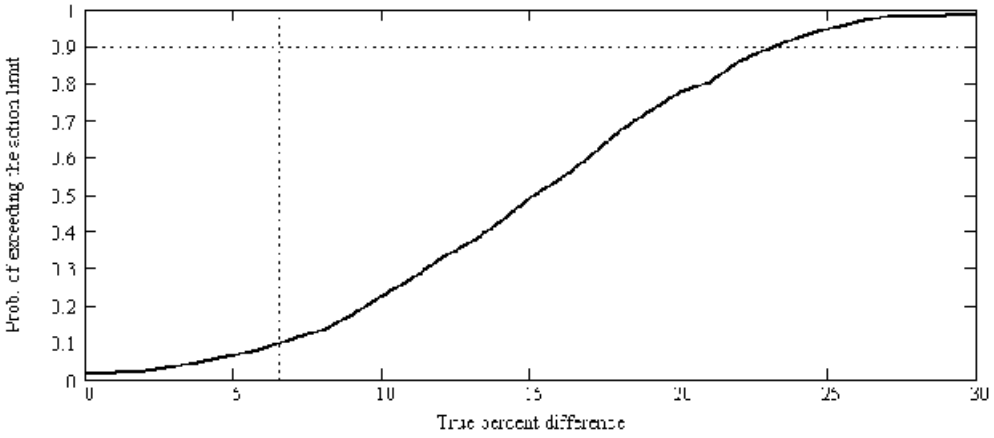

Figure 3.2.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in rural locations of the Pilot Study

3.3 DQOs for Measuring the Percent Decrease of 1,3-Butadiene at Urban Locations

Table 3.3.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at urban locations. Table 3.3.2 shows the output values from the simulations. Figure 3.3.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.3.2 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.3.1 DQO input parameters for 1,3-butadiene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	7.0	100%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.02	37898

Table 3.3.2 DQO output parameters for 1,3-butadiene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
10%	6%	0% - 28%

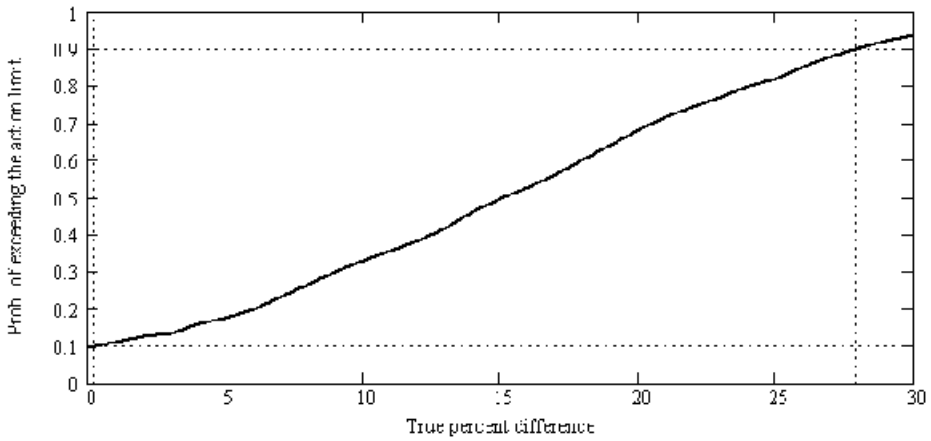

Figure 3.3.1 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in urban locations of the Pilot Study

3.4 DQOs for Measuring the Percent Decrease of 1,3-butadiene at Rural Locations

Table 3.4.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at rural locations. Table 3.4.2 shows the output values from the simulations. Figure 3.4.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.4.2 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.4.1 DQO input parameters for 1,3-butadiene at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3
10%	15%	1 in 6 day	6.0	75%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.02	37898

Table 3.4.2 DQO output parameters for 1,3-butadiene at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
4%	2%	4% - 25%

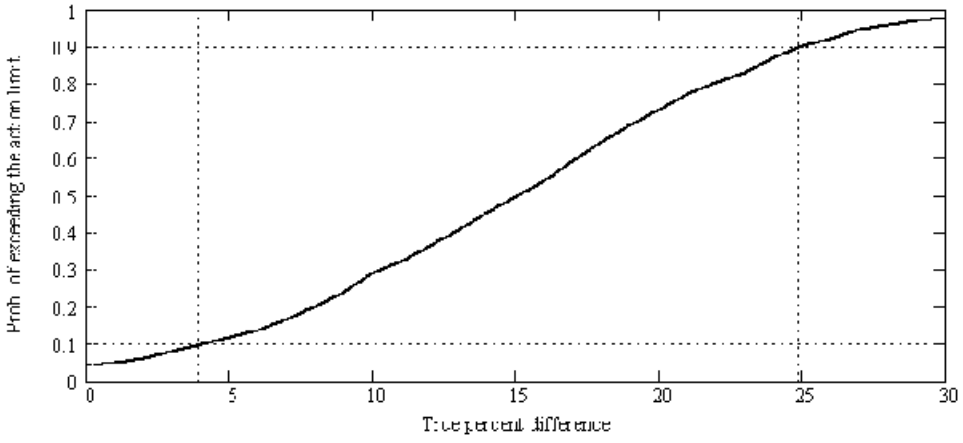

Figure 3.4.1 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in rural locations of the Pilot Study

3.5 DQOs for Measuring the Percent Decrease of Arsenic at Urban Locations

Table 3.5.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at urban locations. Table 3.5.2 shows the output values from the simulations. Figure 3.5.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.5.2 suggests that the specified air toxics trends DQOs will be met for arsenic at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.5.1 DQO input parameters for arsenic at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	5.0	85%	0.002
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.000046	0.0043

Table 3.5.2 DQO output parameters for arsenic at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	5%	2% - 27%

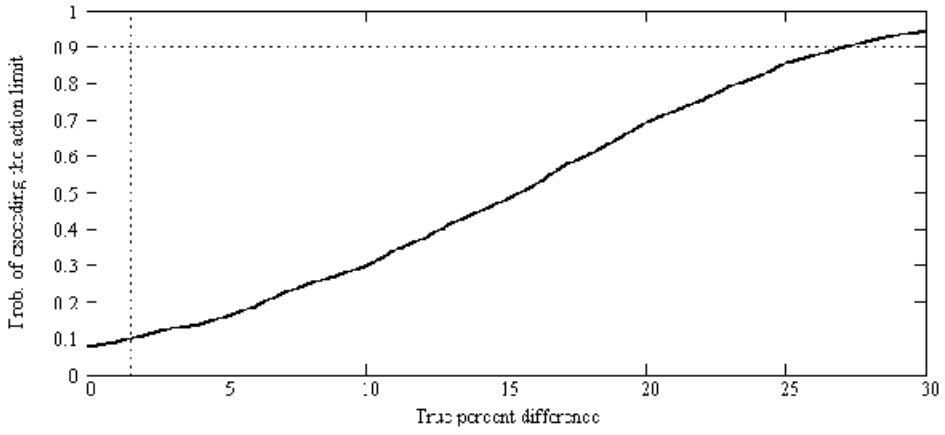

Figure 3.5.1 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in urban locations of the Pilot Study

3.6 DQOs for Measuring the Percent Decrease of Arsenic at Rural Locations

Table 3.6.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at rural locations. Table 3.6.2 shows the output values from the simulations. Figure 3.6.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.6.2 suggests that the specified air toxics trends DQOs will be met for arsenic at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.6.1 DQO input parameters for arsenic at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	4.0	65%	0.001
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.000046	0.0043

Table 3.6.2 DQO output parameters for arsenic at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
3%	1%	5% - 24%

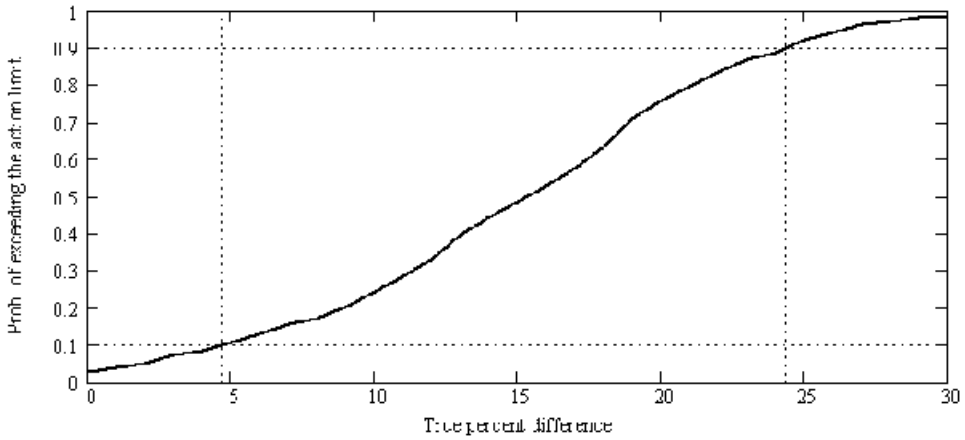

Figure 3.6.1 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in rural locations of the Pilot Study

3.7 DQOs for Measuring the Percent Decrease of Chromium

Table 3.7.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of chromium. Table 3.7.2 shows the output values from the simulations. Figure 3.7.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.7.2 suggests that the specified air toxics trends DQOs will be met for chromium at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.7.1 DQO input parameters for chromium

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	5.0	90%	0.0015
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.00018	0.012

Table 3.7.2 DQO output parameters for chromium

Error rate for no true change	Error rate for 30% decrease	Gray zone
7%	4%	2% - 27%

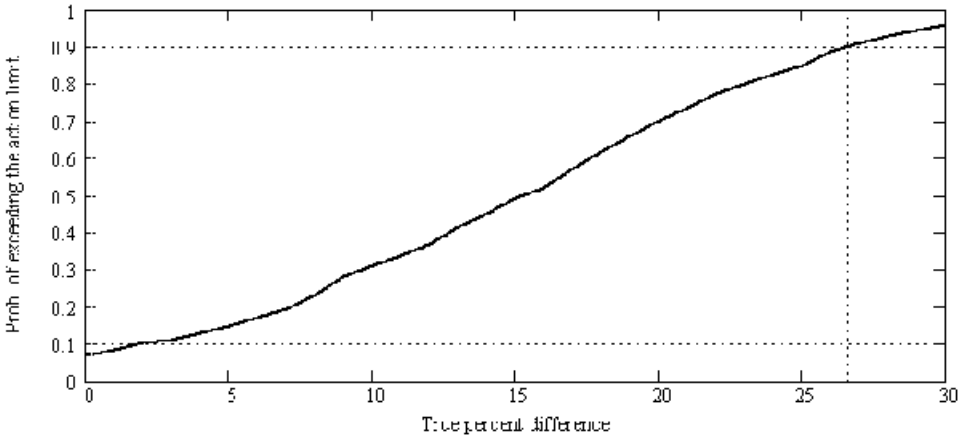

Figure 3.7.1 Power curve for detecting a 15 percent decrease between successive three-year means of chromium concentrations based on the data variation found in of the Pilot Study

3.8 DQOs for Measuring the Percent Decrease of Acrolein

Table 3.8.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of acrolein. Table 3.8.2 shows the output values from the simulations. Figure 3.8.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.8.2 suggests that the specified air toxics trends DQOs will be met for acrolein at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.8.1 DQO input parameters for acrolein

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (mg/m^3)
10%	15%	1 in 6 day	4.0	105%	0.4
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (mg/m^3)**	**Risk Standard (mg/m^3)**
10%	15%	85%	0	0.14	-

Table 3.8.2 DQO output parameters for acrolein

Error rate for no true change	Error rate for 30% decrease	Gray zone
10%	9%	0% - 29%

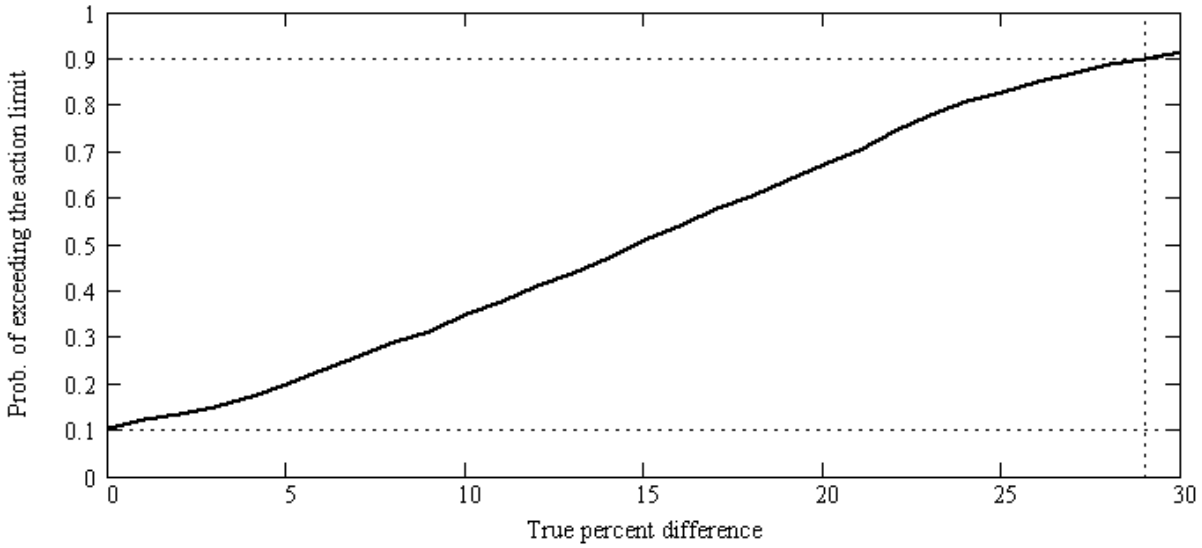

Figure 3.8.1 Power curve for detecting a 15 percent decrease between successive three-year means of acrolein concentrations based on the data variation found in the Pilot Study

3.9 DQOs for Measuring the Percent Decrease of Formaldehyde at Urban Locations

Table 3.9.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at urban locations. Table 3.9.2 shows the output values from the simulations. Figure 3.9.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.9.2 suggests that the specified air toxics trends DQOs will be met for formaldehyde at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See Section 3.0 for definitions of the input parameters and output values.)

Table 3.9.1 DQO input parameters for formaldehyde at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	90%	2.5
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.014	$1.3\ 10^{-5}$

Table 3.9.2 DQO output parameters for formaldehyde at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	5%	2% - 27%

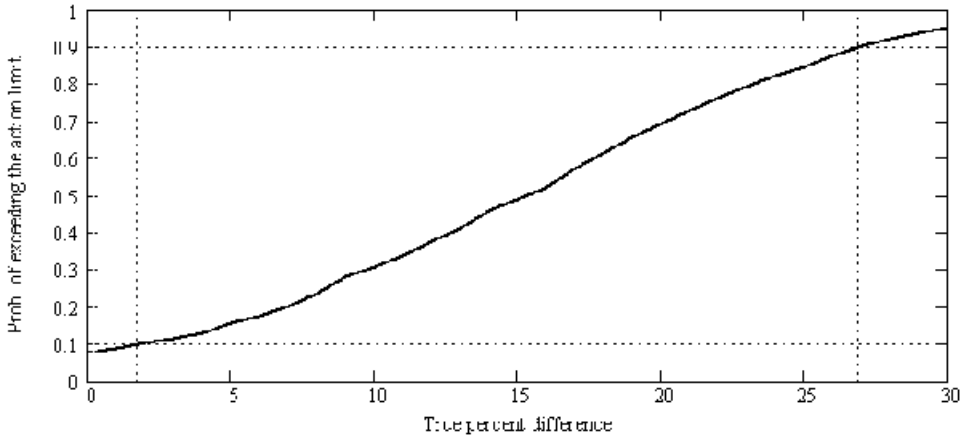

Figure 3.9.1 Power curve for detecting a 15 percent decrease between successive three-year means of formaldehyde concentrations based on the data variation found in urban locations of the Pilot Study

3.10 DQOs for Measuring the Percent Decrease of Formaldehyde at Rural Locations

Table 3.10.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at rural locations. Table 3.10.2 shows the output values from the simulations. Figure 3.10.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.10.2 suggests that the specified air toxics trends DQOs will be met for formaldehyde at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See Section 3.0 for definitions of the input parameters and output values.)

Table 3.10.1 DQO input parameters for formaldehyde at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	90%	2.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.014	$1.3\ 10^{-5}$

Table 3.10.2 DQO output parameters for formaldehyde at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	5%	1% - 27%

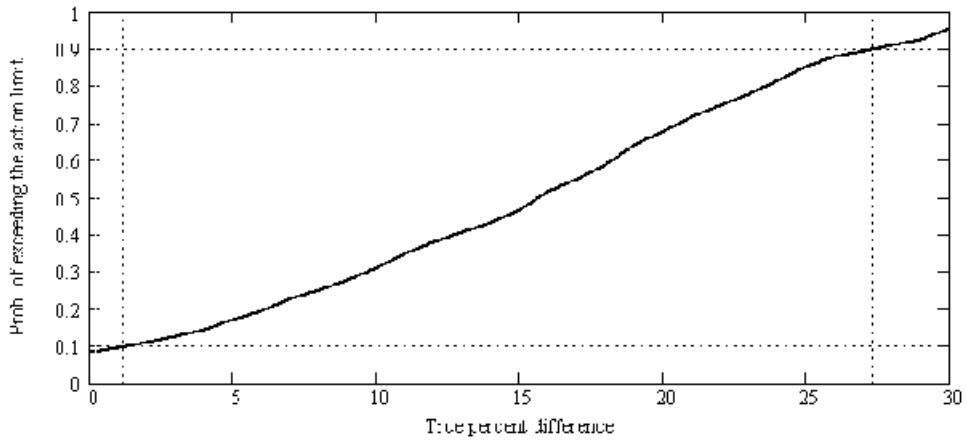

Figure 3.10.1 Power curve for detecting a 15 percent decrease between successive

three-year means of formaldehyde concentrations based on the data variation found in rural locations of the Pilot Study

Attachment 1:

ESTIMATES OF THE DQO PARAMETERS MEASURING ENVIRONMENTAL VARIABILITY

Attachment 1: Estimates of the DQO Parameters Measuring Environmental Variability

The DQO parameters that measure the natural environmental variability of a pollutant are generally uncontrollable parameters that have a strong effect on the decision errors. The simulation model described in Section 2.1 uses these parameters. This appendix describes both the parameters and the method for estimating the parameters from the Pilot data. The basic simulation model is that the true concentration levels vary about a sinusoidal curve with one full oscillation in each year. Four parameters describe characteristics of the sine curve and the natural deviations from the sine curve.

Seasonality Ratio

The ratio parameter is a measure of the degree of seasonality in the data. It is the ratio of the high point to the low point on the sine curve. The model assumes that the amplitude of the sine curve is proportional to the mean. The parameter was estimated by finding the monthly averages and taking the ratio of the highest average to the lowest average. The site estimates are restricted to those sites that had at least 3 measurements in each of at least six months.

Population CV

This parameter measures the amount of random, day-to-day variation of the true concentration about the sine curve. This parameter was estimated as follows. Starting with every 6^{th} day measurements (deleting if needed), the natural log of each measurement was found. Next, a new sequence of numbers was created equal to the differences of successive pairs in the sequence of the log-concentrations that were from measurements taken six days apart. Finally, terms were removed from this sequence so that each term in the remaining sequence was based on distinct numbers. Let S be the standard deviation of this set of numbers. The estimate for the population CV is $\sqrt{\left(\exp\left(S^2/2\right)-1\right)}$. The site estimates are restricted to those with at least ten terms being used in the estimates.

Autocorrelation

The final parameter describing the natural variation of the true concentrations is autocorrelation. This is a measurement of the similarity between successive days. Consider two sets of measurements. First, suppose you had measured the concentrations on every July 15^{th} for the p ast five years. You would expect those five values to be rather spread out. The population CV should capture how different these measurements are from each other. On the other hand, suppose instead you measure the concentrations each day from July 15, 2002, to July 20, 2002. These values may not be as spread out as the other set, simply because they are nearer in time to each other. Autocorrelation measures this effect. A good way to think of

autocorrelation is it measures how quickly the local concentrations can change. The value of the autocorrelation ranges between 0 and 1. A value of 0 means that the local concentrations can change very rapidly from day-to-day. A value of 1 means that the local concentrations are constant.

Estimating autocorrelation is more difficult than estimating the population CV. Unless a site had daily measurements, a value of 0 was used. Realistically, 0 is the most conservative case and can always be used. Assuming a site had daily measurements, let S6 be the standard deviation computed as in the section on population CV, based on differences of the logs from every 6th day measurements. Let *S*1 be the same thing using differences of logs from daily measurements. If *S*6 > *S*1, then the autocorrelation was estimated with $\left(S6^2 - S1^2\right)/S6^2$. This method adjusts for seasonality, but still tends to slightly over estimate the truth. There were too few sites with sufficient daily measurements to obtain distributions of the pollutant autocorrelations, so a value of 0 was used for all pollutants.

Initial concentration.

This is simply the mean concentration for the site.

Table A-1 gives the pollutant and site estimates for the seasonality ratio and the initial mean concentrations. Table A-2 gives the pollutant and site population CV estimates.

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site

Pollutant	Site ID	Urban / Rural	Mean ($\mu g/m^3$)	Seasonality Ratio
1,3-BUTADIENE		Urban	0.3190	3.60
1,3-BUTADIENE	4400700261	Urban	0.2600	3.15
1,3-BUTADIENE	2616300331	Urban	0.2067	2.65
1,3-BUTADIENE	2616300271	Urban	0.2032	2.03
1,3-BUTADIENE	2612500101	Urban	0.2027	1.36
1,3-BUTADIENE	4400700221	Urban	0.1789	5.86
1,3-BUTADIENE	1210300181	Urban	0.1732	4.41
1,3-BUTADIENE	4400700251	Urban	0.1431	4.07
1,3-BUTADIENE	1205710751	Urban	0.1382	5.43
1,3-BUTADIENE	1210310081	Urban	0.1272	3.31
1,3-BUTADIENE	5303300321	Urban	0.1250	6.51
1,3-BUTADIENE	1210350021	Urban	0.1164	2.50
1,3-BUTADIENE	5303300801	Urban	0.1148	5.76
1,3-BUTADIENE	5303300241	Urban	0.1141	7.10
1,3-BUTADIENE	4400700241	Urban	0.1041	4.64
1,3-BUTADIENE	4400710101	Urban	0.1019	5.35
1,3-BUTADIENE	5303300201	Urban	0.1010	10.03
1,3-BUTADIENE	5303300101	Urban	0.0916	10.39
1,3-BUTADIENE	5303300381	Urban	0.0809	5.51
1,3-BUTADIENE	4400300021	Urban	0.0358	5.38
1,3-BUTADIENE	0807700131	Rural	0.2192	6.00
1,3-BUTADIENE	0807700161	Rural	0.1810	4.06
1,3-BUTADIENE	1311300391	Rural	0.1182	3.23
1,3-BUTADIENE	1311300371	Rural	0.0886	1.22
ACROLEIN	4400700261	Urban	0.5904	2.04
ACROLEIN	4400700221	Urban	0.5866	3.36
ACROLEIN	4400700241	Urban	0.5366	2.36
ACROLEIN	4400700251	Urban	0.5366	2.18
ACROLEIN	4400710101	Urban	0.3637	3.34
ACROLEIN	4400300021	Urban	0.3509	3.69
ARSENIC TSP	1205710751	Urban	0.0038	5.01
ARSENIC TSP	2616300271	Urban	0.0033	2.06
ARSENIC TSP	2616300331	Urban	0.0028	3.13
ARSENIC TSP	1210350021	Urban	0.0027	2.94
ARSENIC TSP	1205700811	Urban	0.0027	1.59
ARSENIC TSP	1205710651	Urban	0.0026	1.40
ARSENIC TSP	2616300151	Urban	0.0024	2.68
ARSENIC TSP	1210300181	Urban	0.0024	2.41
ARSENIC TSP	2616300051	Urban	0.0023	2.82
ARSENIC TSP	1210310081	Urban	0.0022	1.56

ARSENIC TSP	2616300011	Urban	0.0021	4.50
ARSENIC TSP	2616300191	Urban	0.0019	2.97
ARSENIC TSP	5303300241	Urban	0.0015	4.48
ARSENIC TSP	2612500101	Urban	0.0014	14.99

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site (Cont'd.)

Pollutant	Site ID	Urban / Rural	Mean $\mu g/m^3$)	Seasonality Ratio
ARSENIC TSP	5303300201	Urban	0.0010	3.80
ARSENIC TSP	5303300381	Urban	0.0009	3.13
ARSENIC TSP	5303300101	Urban	0.0008	4.94
ARSENIC TSP	0807700161	Rural	0.0016	2.11
ARSENIC TSP	0807700131	Rural	0.0008	3.54
BENZENE	2616300271	Urban	18.8411	12.42
BENZENE	2616300051	Urban	2.2038	1.92
BENZENE	2612500101	Urban	2.0860	1.59
BENZENE	2616300331	Urban	2.0710	1.55
BENZENE	5303300321	Urban	1.7124	3.97
BENZENE	5303300241	Urban	1.6500	2.76
BENZENE	4400700261	Urban	1.4416	2.43
BENZENE	1210300181	Urban	1.2763	3.09
BENZENE	4400700221	Urban	1.2648	3.49
BENZENE	5303300801	Urban	1.1697	1.71
BENZENE	5303300101	Urban	1.1466	2.08
BENZENE	5303300381	Urban	1.1161	2.30
BENZENE	4400700251	Urban	1.1123	3.30
BENZENE	1205710751	Urban	1.0364	2.98
BENZENE	5303300201	Urban	1.0229	2.03
BENZENE	1210310081	Urban	0.9283	2.62
BENZENE	1210350021	Urban	0.8940	1.94
BENZENE	4400700241	Urban	0.8849	3.06
BENZENE	1205710651	Urban	0.8791	2.47
BENZENE	4400710101	Urban	0.8006	4.15
BENZENE	1205700811	Urban	0.6451	2.37
BENZENE	4400300021	Urban	0.4190	5.05
BENZENE	0807700131	Rural	2.7088	2.36
BENZENE	0807700161	Rural	1.8649	3.16
BENZENE	1311300391	Rural	1.1701	2.68
BENZENE	0606530111	Rural	1.0166	3.10
BENZENE	1311300371	Rural	0.9221	1.66
BENZENE	0606530121	Rural	0.7622	2.71
CHROMIUM TSP	2616300271	Urban	0.0075	1.70
CHROMIUM TSP	2616300331	Urban	0.0061	1.68
CHROMIUM TSP	2616300151	Urban	0.0059	2.09
CHROMIUM TSP	2616300051	Urban	0.0049	1.90
CHROMIUM TSP	2616300011	Urban	0.0036	2.31
CHROMIUM TSP	2612500101	Urban	0.0034	1.79
CHROMIUM TSP	2616300191	Urban	0.0031	2.45

CHROMIUM TSP	1205710651	Urban	0.0019	1.62
CHROMIUM TSP	1210350021	Urban	0.0017	3.68
CHROMIUM TSP	5303300201	Urban	0.0017	6.25
CHROMIUM TSP	1210300181	Urban	0.0016	2.51

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site (Cont'd.)

Pollutant	Site ID	Urban / Rural	Mean ($\mu g/m^3$)	Seasonality Ratio
CHROMIUM TSP	1205700811	Urban	0.0014	1.87
CHROMIUM TSP	1210310081	Urban	0.0014	2.99
CHROMIUM TSP	1205710751	Urban	0.0014	1.88
CHROMIUM TSP	5303300241	Urban	0.0011	4.23
CHROMIUM TSP	5303300381	Urban	0.0009	3.02
CHROMIUM TSP	5303300101	Urban	0.0009	3.17
FORMALDEHYDE	2616300331	Urban	7.2980	70.55
FORMALDEHYDE	1210300181	Urban	4.1605	2.36
FORMALDEHYDE	4400710101	Urban	4.0325	2.80
FORMALDEHYDE	1205710651	Urban	3.8291	2.25
FORMALDEHYDE	4400700251	Urban	3.6958	2.53
FORMALDEHYDE	2616300271	Urban	3.5940	1.64
FORMALDEHYDE	4400700261	Urban	3.4373	2.36
FORMALDEHYDE	1205700811	Urban	3.4311	2.38
FORMALDEHYDE	4400700221		3.3888	2.01
FORMALDEHYDE	1210310081	Urban	3.2569	2.56
FORMALDEHYDE	1205710751	Urban	2.9991	2.73
FORMALDEHYDE	2612500101	Urban	2.8279	2.21
FORMALDEHYDE	1210350021	Urban	2.8150	2.31
FORMALDEHYDE	2616300191	Urban	2.7887	4.43
FORMALDEHYDE	4400700241	Urban	2.6769	3.25
FORMALDEHYDE	2616300011	Urban	2.4937	2.98
FORMALDEHYDE	5303300801	Urban	1.7148	2.97
FORMALDEHYDE	5303300321	Urban	1.4839	3.56
FORMALDEHYDE	5303300381	Urban	1.3536	2.53
FORMALDEHYDE	5303300201	Urban	1.3236	3.78
FORMALDEHYDE	5303300241	Urban	1.1373	2.48
FORMALDEHYDE	5303300101	Urban	1.0165	9.43
FORMALDEHYDE	0807700131	Rural	7.3046	6.72
FORMALDEHYDE	0807700161	Rural	7.0664	2.15
FORMALDEHYDE	1311300371	Rural	2.3401	5.10
FORMALDEHYDE	1311300391	Rural	2.1613	3.02
FORMALDEHYDE	0606530121	Rural	2.1246	2.83
FORMALDEHYDE	0606530111	Rural	1.6840	1.90

Table A-2. Population CV estimates by pollutant and site

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
1,3-BUTADIENE	530330032	Urban	WA	King County	109.2%
1,3-BUTADIENE	530330024	Urban	WA	King County	106.7%
1,3-BUTADIENE	530330010	Urban	WA	King County	97.4%
1,3-BUTADIENE	530330038	Urban	WA	King County	85.8%
1,3-BUTADIENE	440070025	Urban	RI	Providence County	84.2%
1,3-BUTADIENE	530330020	Urban	WA	King County	79.6%
1,3-BUTADIENE	261630027	Urban	MI	Wayne County	78.0%
1,3-BUTADIENE	261250010	Urban	MI	Oakland County	74.7%
1,3-BUTADIENE	440071010	Urban	RI	Providence County	74.1%
1,3-BUTADIENE	530330080	Urban	WA	King County	72.4%
1,3-BUTADIENE	261630033	Urban	MI	Wayne County	67.8%
1,3-BUTADIENE	121030018	Urban	FL	Pinellas County	67.5%
1,3-BUTADIENE	440070024	Urban	RI	Providence County	64.5%
1,3-BUTADIENE	440070022	Urban	RI	Providence County	63.8%
1,3-BUTADIENE	120571075	Urban	FL	Hillsborough County	62.9%
1,3-BUTADIENE	440070026	Urban	RI	Providence County	61.7%
1,3-BUTADIENE	261630005	Urban	MI	Wayne County	59.5%
1,3-BUTADIENE	121031008	Urban	FL	Pinellas County	57.9%
1,3-BUTADIENE	120571065	Urban	FL	Hillsborough County	57.6%
1,3-BUTADIENE	121035002	Urban	FL	Pinellas County	55.7%
1,3-BUTADIENE	440030002	Urban	RI	Kent County	54.1%
1,3-BUTADIENE	120570081	Urban	FL	Hillsborough County	32.7%
1,3-BUTADIENE	080770013	Rural	CO	Mesa County	69.8%
1,3-BUTADIENE	080770016	Rural	CO	Mesa County	67.1%
1,3-BUTADIENE	131130039	Rural	GA	Fayette County	34.5%
1,3-BUTADIENE	131130037	Rural	GA	Fayette County	13.4%
ACROLEIN	440030002	Urban	RI	Kent County	100.3%
ACROLEIN	440071010	Urban	RI	Providence County	80.7%
ACROLEIN	440070024	Urban	RI	Providence County	66.4%
ACROLEIN	440070022	Urban	RI	Providence County	58.7%
ACROLEIN	440070026	Urban	RI	Providence County	53.4%
ACROLEIN	440070025	Urban	RI	Providence County	39.9%
ARSENIC TSP	530330024	Urban	WA	King County	99.6%
ARSENIC TSP	261630001	Urban	MI	Wayne County	83.8%
ARSENIC TSP	261630019	Urban	MI	Wayne County	78.2%
ARSENIC TSP	261630033	Urban	MI	Wayne County	74.3%
ARSENIC TSP	530330010	Urban	WA	King County	72.1%
ARSENIC TSP	261630005	Urban	MI	Wayne County	68.4%
ARSENIC TSP	530330038	Urban	WA	King County	67.2%
ARSENIC TSP	530330020	Urban	WA	King County	64.0%

ARSENIC TSP	261630027	Urban	MI	Wayne County	64.0%
ARSENIC TSP	261630015	Urban	MI	Wayne County	61.1%
ARSENIC TSP	121035002	Urban	FL	Pinellas County	47.3%
ARSENIC TSP	120571075	Urban	FL	Hillsborough County	44.3%

Table A-2. Population CV estimates by pollutant and site (Cont'd.)

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
ARSENIC TSP	120570081	Urban	FL	Hillsborough County	27.9%
ARSENIC TSP	121031008	Urban	FL	Pinellas County	27.2%
ARSENIC TSP	121030018	Urban	FL	Pinellas County	26.5%
ARSENIC TSP	120571065	Urban	FL	Hillsborough County	22.7%
ARSENIC TSP	080770016	Rural	CO	Mesa County	56.4%
ARSENIC TSP	080770013	Rural	CO	Mesa County	37.0%
BENZENE	261630027	Urban	MI	Wayne County	221.2%
BENZENE	530330032	Urban	WA	King County	93.5%
BENZENE	530330020	Urban	WA	King County	82.2%
BENZENE	530330010	Urban	WA	King County	66.2%
BENZENE	530330024	Urban	WA	King County	64.7%
BENZENE	261630005	Urban	MI	Wayne County	55.1%
BENZENE	121031008	Urban	FL	Pinellas County	49.8%
BENZENE	121030018	Urban	FL	Pinellas County	49.6%
BENZENE	261250010	Urban	MI	Oakland County	48.7%
BENZENE	261630033	Urban	MI	Wayne County	46.2%
BENZENE	440071010	Urban	RI	Providence County	45.8%
BENZENE	121035002	Urban	FL	Pinellas County	41.9%
BENZENE	440070024	Urban	RI	Providence County	41.6%
BENZENE	120571075	Urban	FL	Hillsborough County	41.6%
BENZENE	530330080	Urban	WA	King County	40.1%
BENZENE	530330038	Urban	WA	King County	39.4%
BENZENE	440070025	Urban	RI	Providence County	37.7%
BENZENE	120571065	Urban	FL	Hillsborough County	36.1%
BENZENE	120570081	Urban	FL	Hillsborough County	35.8%
BENZENE	440030002	Urban	RI	Kent County	34.6%
BENZENE	440070022	Urban	RI	Providence County	33.9%
BENZENE	440070026	Urban	RI	Providence County	29.1%
BENZENE	131130037	Rural	GA	Fayette County	54.2%
BENZENE	060653011	Rural	CA	Riverside County	53.7%
BENZENE	131130039	Rural	GA	Fayette County	52.1%
BENZENE	060653012	Rural	CA	Riverside County	49.1%
BENZENE	080770016	Rural	CO	Mesa County	45.8%
BENZENE	080770013	Rural	CO	Mesa County	32.2%
CHROMIUM TSP	530330010	Urban	WA	King County	98.5%
CHROMIUM TSP	530330020	Urban	WA	King County	87.0%
CHROMIUM TSP	530330038	Urban	WA	King County	84.9%
CHROMIUM TSP	530330024	Urban	WA	King County	84.6%
CHROMIUM TSP	121035002	Urban	FL	Pinellas County	61.5%
CHROMIUM TSP	120571065	Urban	FL	Hillsborough County	51.2%
CHROMIUM TSP	120571075	Urban	FL	Hillsborough County	44.6%

CHROMIUM TSP	261630033	Urban	MI	Wayne County	43.9%
CHROMIUM TSP	261630019	Urban	MI	Wayne County	42.7%
CHROMIUM TSP	261630005	Urban	MI	Wayne County	42.0%

Table A-2. Population CV estimates by pollutant and site (Cont'd.)

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
CHROMIUM TSP	261630015	Urban	MI	Wayne County	39.8%
CHROMIUM TSP	121031008	Urban	FL	Pinellas County	39.5%
CHROMIUM TSP	121030018	Urban	FL	Pinellas County	35.6%
CHROMIUM TSP	120570081	Urban	FL	Hillsborough County	34.5%
CHROMIUM TSP	261630027	Urban	MI	Wayne County	33.0%
CHROMIUM TSP	261630001	Urban	MI	Wayne County	31.8%
FORMALDEHYDE	121031008	Urban	FL	Pinellas County	84.9%
FORMALDEHYDE	120570081	Urban	FL	Hillsborough County	80.1%
FORMALDEHYDE	261630033	Urban	MI	Wayne County	78.0%
FORMALDEHYDE	530330032	Urban	WA		72.2%
FORMALDEHYDE	530330024	Urban	WA	King County	59.7%
FORMALDEHYDE	530330020	Urban	WA	King County	57.9%
FORMALDEHYDE	120571075	Urban	FL	Hillsborough County	55.8%
FORMALDEHYDE	530330010	Urban	WA	King County	53.9%
FORMALDEHYDE	440070024	Urban	RI	Providence County	52.3%
FORMALDEHYDE	530330080	Urban	WA	King County	52.2%
FORMALDEHYDE	261630019	Urban	MI	Wayne County	52.0%
FORMALDEHYDE	530330038	Urban	WA	King County	48.9%
FORMALDEHYDE	261630001	Urban	MI	Wayne County	44.0%
FORMALDEHYDE	121035002	Urban	FL	Pinellas County	40.9%
FORMALDEHYDE	120571065	Urban	FL	Hillsborough County	38.2%
FORMALDEHYDE	440070022	Urban	RI	Providence County	37.4%
FORMALDEHYDE	261630027	Urban	MI	Wayne County	35.8%
FORMALDEHYDE	121030018	Urban	FL	Pinellas County	32.7%
FORMALDEHYDE	261250010	Urban	MI	Oakland County	31.1%
FORMALDEHYDE	440070026	Urban	RI	Providence County	28.3%
FORMALDEHYDE	440071010	Urban	RI	Providence County	26.6%
FORMALDEHYDE	440070025	Urban	RI	Providence County	26.6%
FORMALDEHYDE	060653011	Rural	CA	Riverside County	84.3%
FORMALDEHYDE	131130037	Rural	GA	Fayette County	57.2%
FORMALDEHYDE	060653012	Rural	CA	Riverside County	39.3%
FORMALDEHYDE	131130039	Rural	GA	Fayette County	35.1%
FORMALDEHYDE	080770013	Rural	CO	Mesa County	27.6%
FORMALDEHYDE	080770016	Rural	CO	Mesa County	23.7%